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Atmospheric Inputs to the Upper Great Lakes by Dry Deposition Processes

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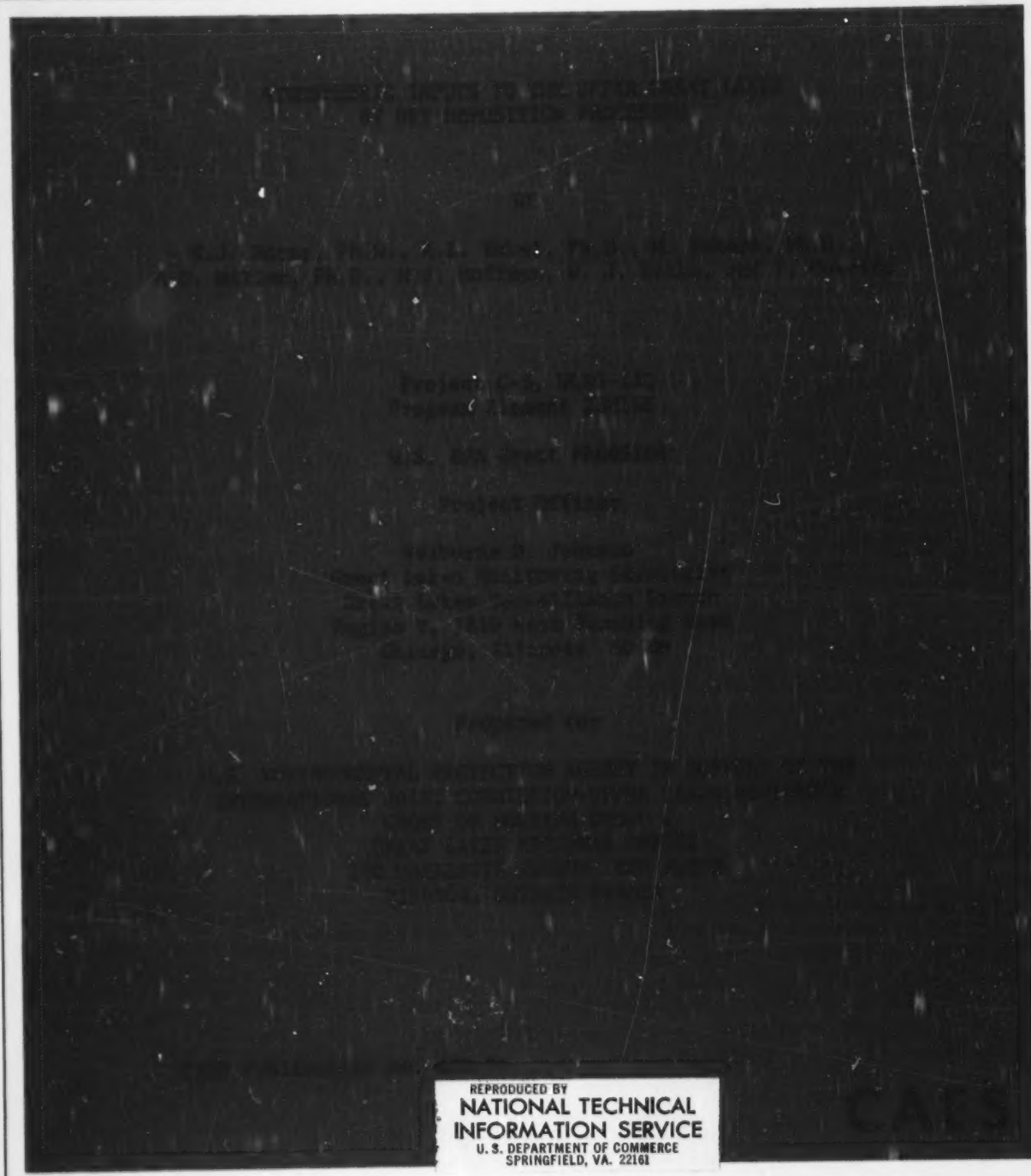

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- Research on effects of air pollutants on trees, food, and fiber crops; predisposition to attack by other pathogens; and economic loss through damage to plants.
- Studies of small particle behavior, particle detectors, and particle collection devices.
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- Research on biological effects of pollutants on animals and vegetation.
- Studies of combustion processes leading to lower contaminant emissions.
- The application of Management Science - Operations Research techniques to the study of the effects of pollution control measures on the decision processes of potential polluters.
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Pollutant removal at a land or water surface by dry deposition processes was accounted for by including a deposition factor in front of the image terms in the conventional Gaussian concentration equation. The inclusion of this deposition factor necessitated a second equation which modeled the flux of material to the surface. Common chemical engineering techniques for modeling mass transfer at a gas-solid or gas-liquid interface were used.

The largest yearly input into the lakes was for chlorides (order of magnitude was 10^5 metric tons/yr.). The second largest input was total dissolved solids with the same order of magnitude input as chlorides. Pesticide input into the Upper Great Lakes from the atmosphere by dry deposition processes was negligible.

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ABSTRACT

A Gaussian plume model was modified to estimate the input of specific atmospheric pollutants into the Upper Great Lakes by dry deposition processes. The specific pollutants were: 1) total dissolved solids, 2) chlorides, 3) total nitrogen, 4) total phosphorus, 5) total silica, and 6) pesticides.

Pollutant removal at a land or water surface by dry deposition processes was accounted for by including a deposition factor in front of the image terms in the conventional Gaussian concentration equation. The inclusion of this deposition factor necessitated a second equation which modeled the flux of material to the surface. Common chemical engineering techniques for modeling mass transfer at a gas-solid or gas-liquid interface were used.

The largest yearly input into the lakes was for chlorides (order of magnitude was 10^5 metric tons/yr.). The second largest input was total dissolved solids with the same order of magnitude input as chlorides. Pesticide input into the Upper Great Lakes by dry deposition processes was negligible.

SUMMARY

A mathematical model was developed to estimate the input of specific airborne pollutants into the Upper Great Lakes by dry deposition processes. The pollutants were: 1) total dissolved solids, 2) chlorides, 3) total nitrogen, 4) total phosphorus, 5) dissolved silica, and 6) pesticides.

The Gaussian plume model coupled with the Pasquill-Gifford diffusion curves formed the foundation for the model. Source strengths were acquired from data compiled by U.S. and Canadian Air Quality Control Regions (AQCR) contained in and around the Great Lakes Basin. Each AQCR was modeled as a point source with an initial crosswind spread.

Dry deposition processes were allowed for by including a deposition factor in front of the reflection term in the conventional Gaussian concentration equation thus permitting less than 100% of the material that reached the ground to be reflected. The inclusion of this deposition factor necessitated a second equation which modeled the flux of material to the surface. The flux of pollutants onto land was modeled as a function of the overall mass transfer coefficient and pollutant concentrations in the atmosphere and the land. Likewise, the flux of pollutants into water was modeled as a function of the liquid phase mass transfer coefficient, the solubility of the pollutant in water, the concentration of the pollutant in

the atmosphere at the interface, and the bulk concentration of the pollutant in the water. The flux equation also differed depending on whether one was considering a gaseous or a particulate pollutant.

Meteorological data compiled at locations over the Great Lakes Basin were used to determine an average yearly wind rose. Seasonal variation of stability conditions over land and water surfaces was included in the model. The total yearly hours of dry weather provided an estimate of the time during which only the dry deposition processes were effective in pollutant removal.

The predictions of pollutant input showed gaseous chlorides (order of 10^5 Mg/Yr) to be the most significant input with total dissolved solids second in terms of quantity ($O(10^5$ Mg/Yr)). Total silica was third ($O(10^4$ Mg/Yr)). Total nitrogen was fourth ($O(10^4$ Mg/Yr)). Total phosphorus was fifth ($O(10^3$ Mg/Yr)) and pesticides were least with only 3 Mg/Yr predicted to enter each Upper Great Lake from the atmosphere by dry deposition processes. The input into Huron was 1.5 times the input into Superior for every pollutant with two exceptions. The input of pesticides into Huron was 1.1 times the input into Superior and the input of total nitrogen into Huron was 1.9 times the input into Superior.

CHAPTER 1

INTRODUCTION

It is possible that pollutants transported through the atmosphere and deposited into the waters of the Upper Great Lakes could contribute significantly to the pollutant loading of the lakes. Such deposition can occur during precipitation events or by the vertical transport of gases and particles. The introduction of pollutants into the lakes by surface mechanisms and by precipitation scavenging is the topic of other International Joint Commission (IJC) efforts. This report is concerned only with gaseous and particulate deposition.

PROJECT OBJECTIVES

The specific objectives of this study are: 1) to develop a numerical model which will permit estimation of the contamination of a water body by airborne pollutants during dry meteorological conditions, and 2) to use this model to provide estimates of the potential contribution from the atmosphere to the whole lake burden in the Upper Great Lakes. The pollutants of interest are total dissolved solids, chlorides, total nitrogen, total phosphorous, dissolved silica and pesticides.

GENERAL DEFINITIONS

Definition Of The Upper Great Lakes

Reference is made frequently to the Upper Great Lakes. This term includes two lake regions: 1) Lake Superior, and 2) Lake Huron including the North Channel and the Georgian Bay.

Air Quality Control Regions Near The Great Lakes Basin

The divide marking the Great Lakes Basin encompasses a portion of seven states and the Canadian province of Ontario and all the state of Michigan. The seven states are: New York, Pennsylvania, Ohio, Indiana, Illinois, Minnesota, and Wisconsin. The divide is never farther than 125 miles from the nearest point on one of the lake shores. The Great Lakes Basin is shown in Figure 1.1 (Phillips & McCulloch, 1972).

Each of the states comprising the Great Lakes Basin is divided into Air Quality Control Regions (AQCR). Each AQCR represents a pollutant source and the two Upper Great Lakes represent pollutant receptors. The problem consists in quantifying the pollutant input into the Upper Great Lakes.

REPORT FORMAT

The report begins with the presentation of the atmospheric transport and deposition model. This is followed by the details of how the model is applied to the problem at hand. Next, the methodology used to attain the input parameters is discussed. The procedures to estimate the input of each individual chemical species into the Upper Great Lakes are then considered in turn. Finally, the results are presented.

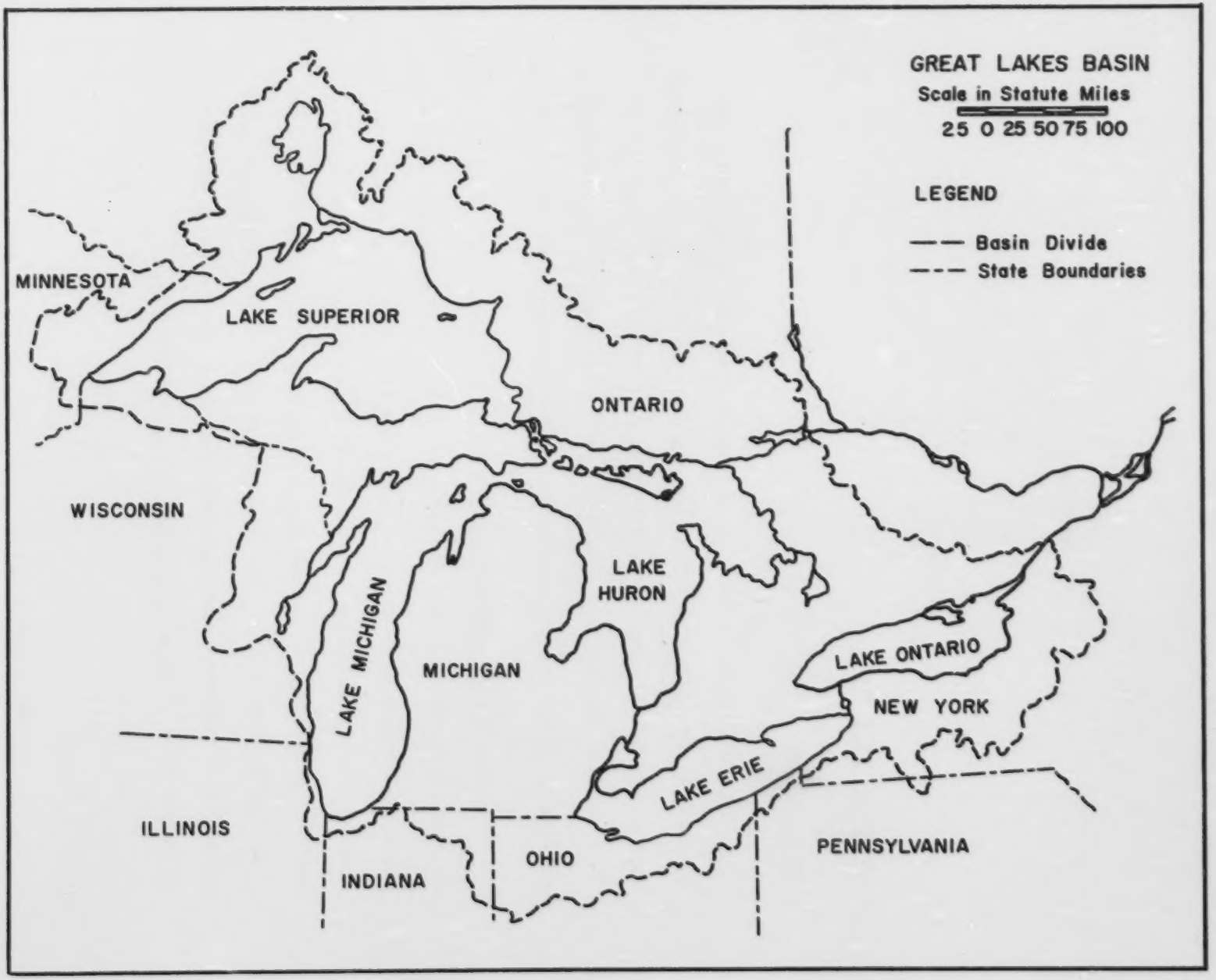

Figure I.1: Great Lakes Basin

CHAPTER 2

THE THEORETICAL MODEL

INTRODUCTION

The Gaussian plume model has for years been the primary device for estimating air quality relative to the source location and emission rates. It has been called upon in the making of critical air quality decisions. These include forecasting of undesirable levels of pollution, abatement strategies, long range air resource management programs and urban planning.

Gaussian plume models in the present form (Sutton, 1953; Turner, 1970) are considered to be useful to predict the air pollution level, when the ground is assumed to be a perfect reflector or a perfect sink. In reality however, various pollutants may be absorbed or produced by the sundry surfaces comprising the ground at a limited rate (Rasmussen, Taheri, and Kabel, 1975; Hidy, 1973). The objective of this section is to present a mathematical treatment that considers the effect of absorption or desorption at ground level on plume dispersion and flux distribution.

PHYSICAL & MATHEMATICAL MODEL

The Diffusion Equation And Its Solution

The Gaussian distribution function is a fundamental solution of the following simplified diffusion equation

$$u \frac{\partial C}{\partial x} = K_z \frac{\partial^2 C}{\partial z^2} + K_y \frac{\partial^2 C}{\partial y^2} \qquad 2.1$$

where u is downwind mean velocity, C is the mean concentration, x is the downwind direction, y is the crosswind direction, z is the vertical direction K_z is the vertical eddy diffusion coefficient, and K_y is the crosswind eddy diffusion coefficient. The simplifying assumptions necessary to write the diffusion equation in the form of Equation 2.1 are:

1) steady conditions
2) K_z is not a function of z
3) K_y is not a function of y
4) there is no extraction of pollutant
5) the downwind transport greatly exceeds the downwind diffusion.

The system to be considered is shown in Figure 2.1 and has been described in detail by Somers (1971). The solution for a pollutant continuously released in an infinite medium from a point source of strength Q at x = y = 0 and z = h is given by (Sutton, 1953) and (Pasquill, 1962) as:

$$C = \frac{Q}{2\pi\sigma_y\sigma_z u} \left(\exp\left(-1/2 \left(\frac{y^2}{\sigma_y^2} + \frac{(z-h)^2}{\sigma_z^2}\right)\right)\right) \qquad 2.2$$

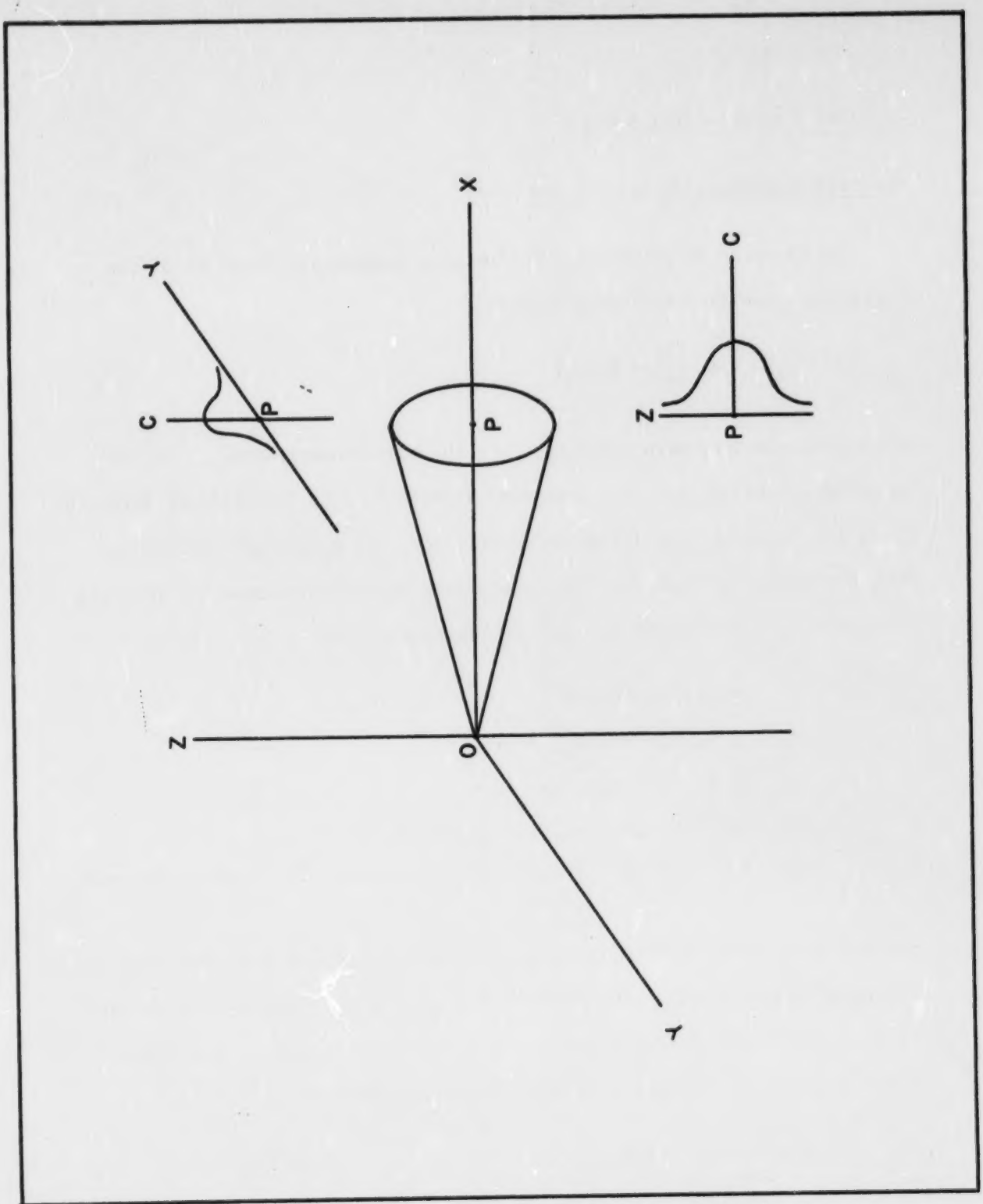

Figure 2.1: The Point Source and the Gaussian Plume (Somers, 1971).

where σ_y and σ_z are referred to as dispersion coefficients in the y and z directions and are related to the eddy diffusion coefficients by the following equation (expressed in tensor notation):

$$\sigma_i = \sqrt{2 \times K_i / u} \qquad 2.3$$

Equation 2.2 assumes that the windspeed is not a function of height.

Description of the concentration to include ground reflection is obtained by use of the method of images (Somers, 1971). This consists of establishing an image source of strength Q at x = y = 0 and z = -h and adding the solutions for both the image and real source to yield:

$$C = \frac{Q}{2\pi\sigma_y\sigma_z u} \left(\exp\left(-1/2 \left(\frac{y^2}{\sigma_y^2} + \frac{(z-h)^2}{\sigma_z^2}\right)\right) + \exp\left(-1/2 \left(\frac{y^2}{\sigma_y^2} + \frac{(z+h)^2}{\sigma_z^2}\right)\right)\right) \qquad 2.4$$

Equation 2.4 satisfies the boundary condition of no flux at ground level or

$$\frac{\partial C}{\partial z}\Big|_{z=0} = 0$$

For a perfect sink yielding a concentration of zero at the ground level, a similar method is used. This consists of establishing a source of strength Q at x = y = 0 and z = -h and subtracting the solution of the sink-image from the solution of the real source:

$$C = \frac{Q}{2\pi\sigma_y\sigma_z u} \left(\exp\left(-1/2 \left(\frac{y^2}{\sigma_y^2} + \frac{(z-h)^2}{\sigma_z^2}\right)\right) - \exp\left(-1/2 \left(\frac{y^2}{\sigma_y^2} + \frac{(z+h)^2}{\sigma_z^2}\right)\right)\right) \qquad 2.5$$

This solution satisfies the boundary condition of C = 0 at z = 0.

Evidence is mounting that surfaces on the ground level such as grass, water, and soil do not act as a perfect reflector or a perfect sink. They absorb various pollutants with a given rate based on mass transfer coefficients, solubility data, and concentrations of the pollutants contained in the receptors. In the following section a mathematical model is developed for considering the effect of real surfaces on the dispersion of pollutants in the atmosphere.

Extension Of A Gaussian Plume Model To A Real Surface

For a plume in which absorption or desorption occurs with a given rate the following general equation is considered

$$C = \frac{Q}{2\pi\sigma_y\sigma_z u}\left(\exp\left(-\tfrac{1}{2}\left(\frac{y^2}{\sigma_y^2}+\frac{(z-h)^2}{\sigma_z^2}\right)\right) - \gamma\exp\left(-\tfrac{1}{2}\left(\frac{y^2}{\sigma_y^2}+\frac{(z+h)^2}{\sigma_z^2}\right)\right)\right) \qquad 2.6$$

where γ is a correction factor and may change from (1) for perfect sink to (-1) for perfect reflection and less than (-1) for desorption processes.

The specification of absorption at ground level as a boundary condition establishes whether the surface acts as a sink or source or a perfect reflector. In order to determine γ, the continuity of fluxes in the gas phase and the ground level surface is used as a boundary condition:

$$K_z \frac{\partial C}{\partial z}\Big|_{z=0} = k\,(C_{a|z=0} - C_{ab}) \qquad 2.7$$

where C is the gas phase concentration of the pollutant species, k is the absorbing phase mass transfer coefficient, $C_{a|z=0}$ is the concentration of the pollutant on the absorbing phase side of the interface, and C_{ab} is the bulk concentration of the pollutant in the absorbing phase. Rewriting Equation 2.3 in terms of K_z yields

$$K_z = \frac{\sigma_z^2 u}{2x} \qquad 2.8$$

Equations 2.7 and 2.8 thus provide the relationship for applying the continuity of fluxes across the exposed surfaces where these surfaces are not passive to the transport of pollutants. Transport over a water surface is the easiest to describe since the absorption coefficient, k_ℓ, and the liquid bulk concentration are more easily defined and available than for many other cases such as transport over soil or a vegetation region. Therefore, the transport over water and land will be treated separately.

Transport Over Water Surfaces

For an absorbing-desorbing surface of water and for sufficiently dilute systems, Henry's law can be used to relate the gas phase and liquid phase concentrations at the interface:

$$C_\ell|_{z=0} = \frac{C|_{z=0}}{H} \qquad 2.9$$

where H is the Henry's law constant. For a number of gases H can be found in Perry's Chemical Engineers' Handbook (1963).

Upon substitution of Equations 2.8 and 2.9 into Equation 2.7 one can obtain

$$\frac{\sigma^2_z u}{2x} \left.\frac{\partial C}{\partial z}\right|_{z=0} = k_\ell \left(\frac{C|_{z=0}}{H} - C_{\ell b}\right) \qquad 2.10$$

Where $C_{\ell b}$ is the bulk liquid phase concentration and k_ℓ is the liquid phase mass transfer coefficient. Representative values of k_ℓ can be found in the literature or predicted. For example, see Heines and Peters (1974), Liss and Slater (1974), and Kabel (1975). Substituting the general equation of concentration distribution (Equation 2.6) into both sides of Equation 2.10 yields:

$$\frac{Qh(1+\gamma)}{4\pi\sigma_y\sigma_z x} \exp\left(-1/2\left(\frac{y^2}{\sigma_y^2} + \frac{h^2}{\sigma_z^2}\right)\right) = \frac{k_\ell}{H} \frac{Q(1-\gamma)}{2\pi\sigma_y\sigma_z u} \cdot \exp\left(-1/2\left(\frac{y^2}{\sigma_y^2} + \frac{h^2}{\sigma_z^2}\right)\right) - k_\ell C_\ell \qquad 2.11$$

Now the value of γ can be determined from Equation 2.11:

$$\gamma = \frac{B-A - k_\ell C_{\ell b}}{A+B} \qquad 2.12$$

where

$$A = \frac{Qh}{4\pi\sigma_y\sigma_z x} \exp\left(-1/2\left(\frac{y^2}{\sigma_y^2} + \frac{h^2}{\sigma_z^2}\right)\right)$$

$$B = \frac{k_\ell Q}{2\pi H\sigma_y\sigma_z u} \exp\left(-1/2\left(\frac{y^2}{\sigma_y^2} + \frac{h^2}{\sigma_z^2}\right)\right)$$

Upon substitution of γ in Equation 2.11, one can obtain

$$\text{Flux} = F = \frac{Qh(2B-k_\ell C_{\ell b})}{4\pi(A+B)\sigma_y\sigma_z x} \exp\left(-1/2\left(\frac{y^2}{\sigma_y^2} + \frac{h^2}{\sigma_z^2}\right)\right) \qquad 2.13$$

For $C_{\ell b}$, the bulk concentration in the liquid phase, larger than interfacial concentration, the numerical value of γ becomes less than (-1) and the flux is from the liquid to the gas phase. For $C_{\ell b}$ equal to zero, Equation 2.12 is simplified to

$$\gamma = \left(\frac{k_\ell}{H} - \frac{hu}{2x}\right) / \left(\frac{k_\ell}{H} + \frac{hu}{2x}\right) \qquad 2.14$$

Equation 2.14 indicates the value of γ is a function of x. A similar trend is reported by Johnstone et al. (1949) and Cuscino et al. (1975) for particle deposition using an overall material balance approach.

Transport Over Land

The development of rate processes over land is in its primitive stage. The bulk and interfacial concentrations are unknown. Very often the flux is given in terms of deposition velocity (Chamberlain, 1960; Spedding, 1969; Owers and Powell, 1974; Hill, 1971)

$$K_z \frac{\partial C}{\partial z}\Big|_{z=0} = (V_d C)\Big|_{z = \text{reference height}} \qquad 2.15$$

where V_d is the deposition velocity and is a function of the type of surface.

A more realistic approach is to write Equation 2.15 in terms of an overall mass transfer coefficient:

$$K_z \frac{\partial C}{\partial z}\Big|_{z=0} = K_g (C_b - C_b^*) \qquad 2.16$$

where K_g is an overall mass transfer coefficient which is a function of both the gas and the land mass transfer coefficients, C_b is the bulk gas phase concentration and $C_b^* = H\, C_{ab}$ where C_{ab} is the bulk land phase concentration. For a special case where $C_{ab}=0$ and C_b is equal to the $C|_{z}$ = reference height, Equation 2.16 would become identical to the familiar Equation 2.15 and K_g would equal V_d. Furthermore, if the reference height is taken as the ground level, one obtains the following equation

$$K_z \frac{\partial C}{\partial z}\Big|_{z=0} = (V_d C)\Big|_{z=0} \qquad 2.17$$

Again both sides of Equation 2.17 can be evaluated from the general Equation 2.6 to solve for γ as follows:

$$\gamma = (V_d - \frac{hu}{2x}) / (V_d + \frac{hu}{2x}) \qquad 2.18$$

The vertical flux of a gas transported over land can then be expressed

$$F = K_z \frac{\partial C}{\partial z}\Big|_{z=0} = \frac{Qh}{2\pi \sigma_y \sigma_z x} \left(\frac{V_d}{V_d + \frac{hu}{2x}}\right) \exp\left(-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2} + \frac{h^2}{\sigma_z^2}\right)\right) \qquad 2.19$$

For general cases where more information is available on the rate process over the land surfaces one can apply a similar treatment as over water and obtain a more generalized equation for both concentration and flux distribution.

Extension To An Inversion Trap

Another condition of interest is the effect of an inversion layer on the concentration profile. Friedlander and Seinfeld (1969) and Sklarew (1970) have included the effect of an inversion layer in a numerical

approach to the problem. Heines and Peters (1973) presented an analytical solution with no mass flux or absorption at ground level. Somers (1971) presented the solution for an inversion trap using the method of images for multiple reflections. What follows is a modified image method for a case of inversion with limited absorption or desorption on the ground level.

As shown in Figure 2.2, let the source be located at $x = y = 0$, $z = h$, with an inversion layer reflecting at $z = H'$. For simplicity only the first inversion reflection is considered. The plume is now trapped between two reflecting surfaces. The upper edge of the plume is reflected first at 1 and then at 2 while the lower edge is reflected successively at 3, 4, and 5. The image sources are mathematical constructs to fulfill the physical premise that no material is lost from between the two reflecting surfaces. When the ground is not viewed as a perfect reflector, then the image sources below the ground carry a correction factor of γ. The concentration is given as the sum of the pollutant input from all the sources:

$$C = \frac{Q}{2\pi\sigma_y\sigma_z u} \exp\left(-\left(\frac{y^2}{2\sigma_y^2}\right)\right) \left\{\exp\left(-\left(\frac{(z-h)^2}{2\sigma_z^2}\right)\right) - \gamma \exp\left(-\left(\frac{(z+h)^2}{2\sigma_z^2}\right)\right) + \right.$$

$$\exp\left(-\tfrac{1}{2}\left(\frac{(z-2H+h)^2}{\sigma_z^2}\right)\right) + \exp\left(-\tfrac{1}{2}\left(\frac{(z-2H'-h)^2}{\sigma_z^2}\right)\right) - \gamma \exp\left(-\tfrac{1}{2}\left(\frac{(z+2H+h)^2}{\sigma_z^2}\right)\right)$$

$$\left. - \gamma \exp\left(-\tfrac{1}{2}\left(\frac{(z+2H'-h)^2}{\sigma_z^2}\right)\right)\right\} \qquad 2.20$$

In order to determine γ, the equality of the pollutant flux leaving the gas phase at $z=0$ and entering the absorbing phase at $z=0$ is used as a boundary condition over a water surface, the equality can be expressed as

$$K_z \frac{\partial C}{\partial z}\Big|_{z=0} = k_\ell \left(\frac{C|_{z=0}}{H} - C_\ell\right) \qquad 2.21$$

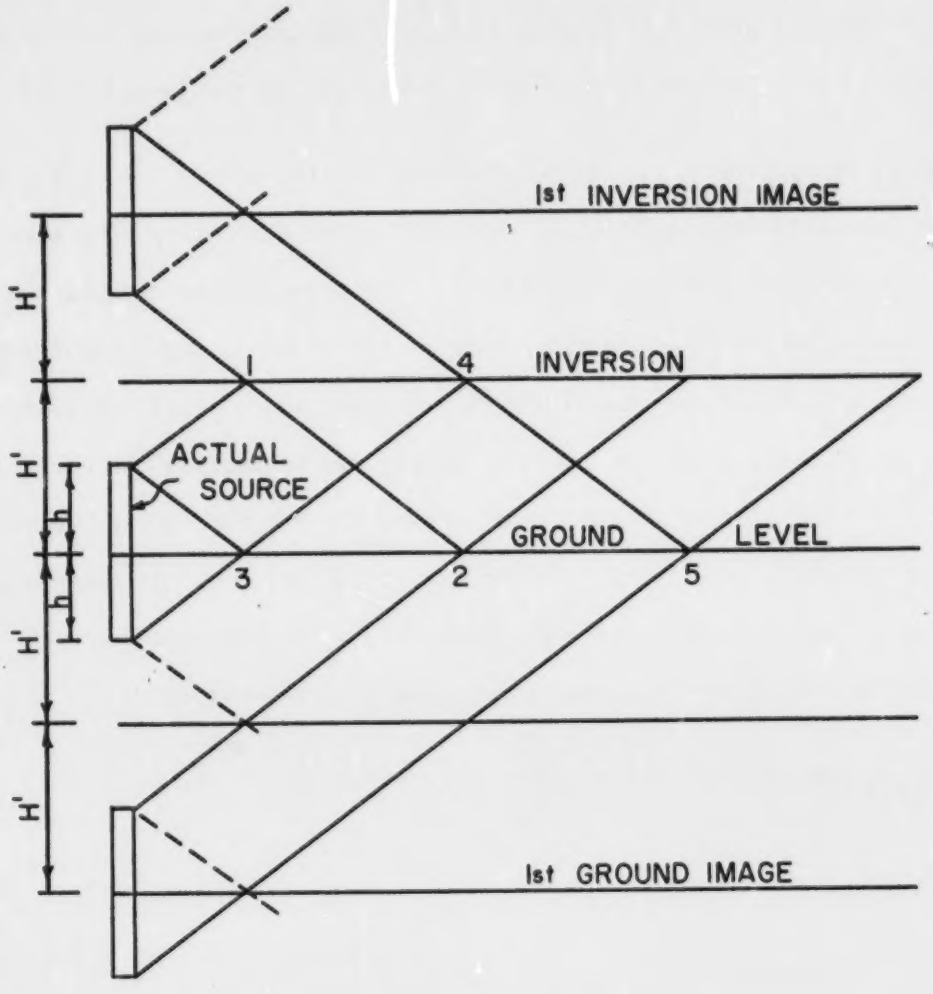

Figure 2.2: A Sketch of the Image Sources Used to Mathmatically Allow for Reflections in an Inversion Trap (Somers, 1971).

Upon substitution from Equation 2.20 to Equation 2.21 one obtains:

$$\frac{Q}{4\pi\sigma_y\sigma_z x}\exp\left(-\left(\frac{y^2}{2\sigma_y{}^2}\right)\right)\left(h\exp\left(-1/2\left(\frac{h^2}{\sigma_z{}^2}\right)\right)+h\gamma\exp\left(-1/2\left(\frac{h^2}{\sigma_z{}^2}\right)\right)\right.$$

$$-(h-2H')\exp\left(-1/2\left(\frac{(h-2H')^2}{2\sigma_z{}^2}\right)\right)+(2H'+h)\exp\left(-1/2\left(\frac{(2H'+h)^2}{\sigma_z{}^2}\right)\right.$$

$$+\gamma(2H'+h)\exp\left(-1/2\left(\frac{(2H'+h)^2}{\sigma_z{}^2}\right)\right)+\gamma(2H'-h)\exp\left(-1/2\left(\frac{(2H'-h)^2}{\sigma_z{}^2}\right)\right)\Big)$$

$$=\frac{k_\ell Q}{2\pi H\sigma_z\sigma_y u}\exp\left(-1/2\left(\frac{y^2}{\sigma_y{}^2}\right)\right)\left((1-\gamma)\exp\left(-1/2\left(\frac{h^2}{\sigma_z{}^2}\right)\right)+\right.$$

$$(1-\gamma)\exp\left(-1/2\left(\frac{(2H'-h)^2}{\sigma_z{}^2}\right)\right)+(1-\gamma)\exp\left(-1/2\left(\frac{(2H'+h)^2}{\sigma_z{}^2}\right)\right)\Big)-k_\ell C_\ell \qquad 2.22$$

Solving for γ from Equation 2.22 yields

$$\gamma=\frac{M'-M+N'-N+O'-O-k_\ell C_\ell}{M'+M+N'+N+O'+O} \qquad 2.23$$

where

$$M=\frac{Q\,h}{4\pi\sigma_y\sigma_z x}\exp\left(-\left(\frac{y^2}{2\sigma_y{}^2}\right)\right)\exp\left(-\left(\frac{h^2}{2\sigma_z{}^2}\right)\right)$$

$$N=\frac{Q\,(2H'-h)}{4\pi\sigma_y\sigma_z x}\exp\left(-\left(\frac{y^2}{2\sigma_y{}^2}\right)\right)\exp\left(-1/2\left(\frac{(2H'-h)^2}{\sigma_z{}^2}\right)\right)$$

$$O=\frac{Q\,(2H'+h)}{4\pi\sigma_y\sigma_z x}\exp\left(-\left(\frac{y^2}{2\sigma_y{}^2}\right)\right)\exp\left(-1/2\left(\frac{(2H'+h)^2}{\sigma_z{}^2}\right)\right)$$

$$M'=\frac{QK'}{2\pi\sigma_z\sigma_y u}\exp\left(-\left(\frac{y^2}{2\sigma_y{}^2}\right)\right)\exp\left(-\left(\frac{h^2}{2\sigma_z{}^2}\right)\right)$$

$$N'=\frac{QK'}{2\pi\sigma_z\sigma_y u}\exp\left(-\left(\frac{y^2}{2\sigma_y{}^2}\right)\right)\exp\left(-1/2\left(\frac{(2H'-h)^2}{\sigma_z{}^2}\right)\right)$$

$$C' = \frac{QK'}{2\pi\sigma_z\sigma_y u} \exp\left(-\left(\frac{y^2}{2\sigma_y^2}\right)\right) \exp\left(-1/2\left(\frac{(2H' + h)^2}{\sigma_z^2}\right)\right)$$

$$K' = \begin{cases} \frac{k_\ell}{H} & \text{for gas} \\ V_d & \text{for particles (if considering particles, delete } k_\ell C_\ell \text{ in Equation 2.23)} \end{cases}$$

In order to obtain the flux, the value of γ obtained from Equation 2.23 is substituted in either side of the following equation:

$$F = \frac{Q}{4\pi\sigma_y\sigma_z x} \exp\left(-\left(\frac{y^2}{2\sigma_y^2}\right)\right) \left(h\,(1 + \gamma) \exp\left(-\left(\frac{h^2}{2\sigma_z^2}\right)\right) + (2H' - h)\right.$$

$$\left.(1 + \gamma) \exp\left(-\left(\frac{(2H - h)^2}{2\sigma_z^2}\right)\right) + (2H' + h)\,(1 + \gamma) \exp\left(-\left(\frac{(2H' + h)^2}{2\sigma_z^2}\right)\right)\right)$$

2.24

DETERMINATION OF k_ℓ AND H

The liquid phase mass transfer coefficient, k_ℓ, and Henry's law constant, H, are parameters which characterize the resistance of the liquid phase to the uptake of mass. They are necessary to quantify the natural mechanism of removal of atmospheric pollutants by water bodies. In most of the previous efforts to develop air pollution models, water bodies have been assumed to be perfect sinks or perfect reflectors of atmospheric pollutants. These are limiting cases in which the liquid phase offers no resistance to pollutant uptake or infinite resistance to pollutant uptake. Under these conditions, the solubility of the pollutant in the liquid phase and the liquid phase mass transfer coefficient have their limiting values which can be specified. For the perfect sink, either the pollutant is

infinitely soluble or the liquid mass transfer coefficient is infinity. For the perfect reflector, either the pollutant is insoluble or the liquid phase mass transfer coefficient is zero. Although the limiting cases can simplify the situation, in reality atmospheric pollutants can be absorbed by or desorbed from bodies of water at finite rates (Rasmussen, et al, 1974). Therefore, the pollutant solubility in water and the liquid phase mass transfer coefficient must be considered in more detail.

The pollutant solubility in water, which is species dependent, can be determined experimentally at various temperatures, pressures and pollutant concentration levels. This is essentially an equilibrium determination in which the liquid phase concentration of solute is determined as a function of temperature, pressure and gas phase concentration. In many cases, a correlation can be obtained relating the gas phase concentration to the liquid phase concentration. This is accomplished by using the Henry's Law constant, which is a measure of solubility. The definition of the Henry's Law constant is

$$H = \frac{C_{gi}}{C_{\ell i}} \qquad 2.25$$

where C_{gi} is the interfacial equilibrium concentration of the species in the gas phase and $C_{\ell i}$ is the interfacial equilibrium concentration of the species in the liquid phase.

The liquid phase mass transfer coefficient, which is also species dependent, can be defined as

$$k_{\ell} = \frac{F_{\ell}}{C_{\ell i} - C_{\ell b}} \qquad 2.26$$

where F_ℓ is the mass flux of the species through the liquid, $C_{\ell i}$ is the interfacial concentration of the species in the liquid and $C_{\ell b}$ is the concentration of the species in the bulk liquid phase. Many attempts have been made to develop models to determine the liquid phase mass transfer coefficient. For example, see Whitman (1923), Higbie (1935), and Danckwerts (1951). These models retain one basic limitation. While they may be capable of interpreting important experimental observations, great difficulties remain in using them to predict liquid phase mass transfer coefficients. This is due to the fact that all of them contain one or more arbitrary parameters which cannot be specified a priori from the experimental conditions of a situation of interest. To resolve this problem, Fortescue and Pearson (1967) and Lamont and Scott (1970) developed models which contain parameters that can be obtained from physical quantities characteristic of the turbulent flow field. These are the large eddy model and the eddy cell model, respectively.

Before discussing the models, it is necessary to give a physical picture of a water body. Figure 2.3 depicts a water body bounded vertically by a free liquid surface and the water body bottom. It is also assumed that there is a mixed region and a stagnant region separated by a thermocline. This stratification does not occur in all bodies of water, but in large lakes and oceans, it will exist in many situations. It has been observed that airflow over water bodies induces a roll cell behavior in the liquid near the surface, as shown in Figure 2.4. These concepts are assumed in the models that follow.

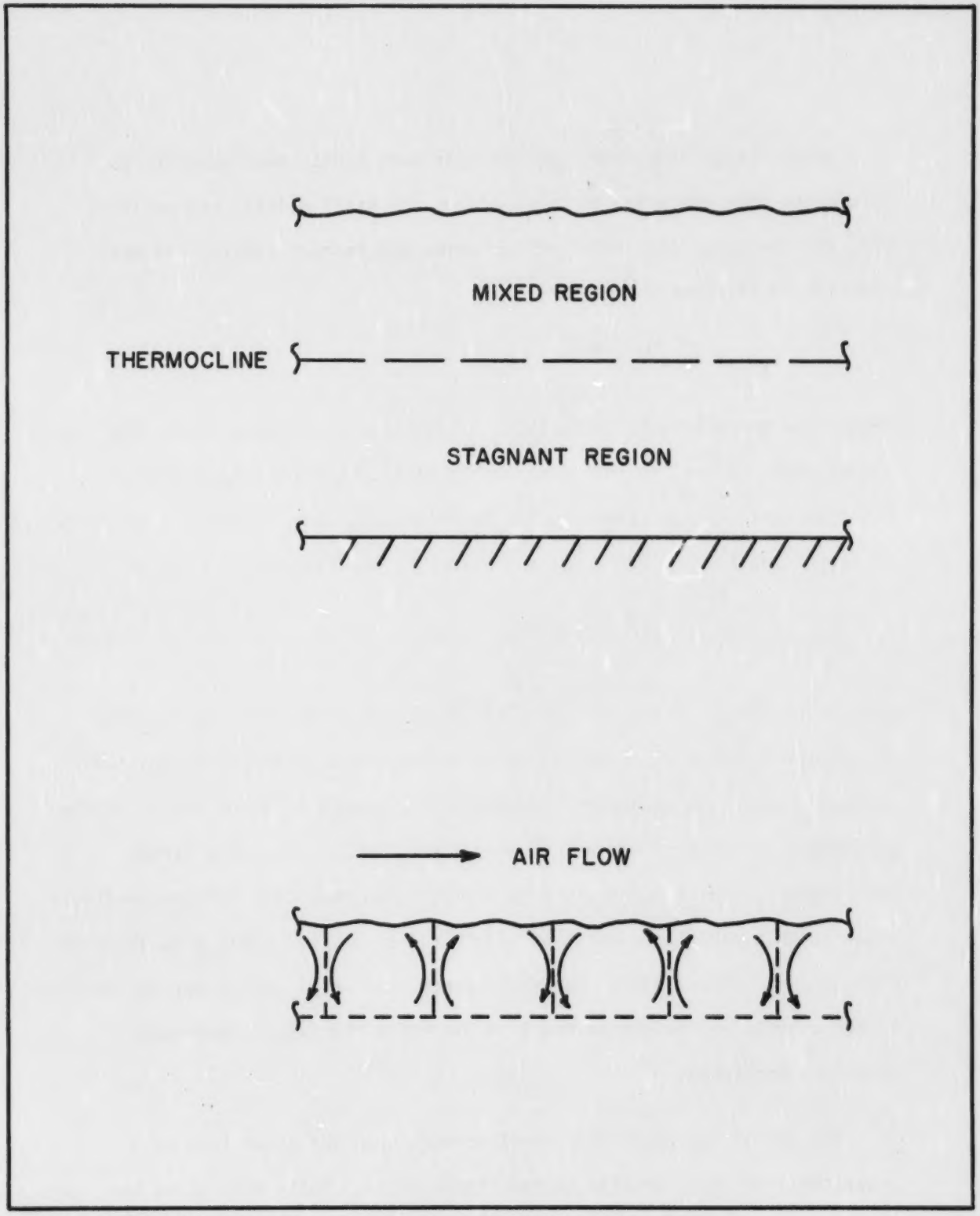

Figure 2.3 (Top): Schematic Diagram of a Stratified Water Body
Figure 2.4 (Bottom): Wind Induced Roll Cells

In the large eddy model and the eddy cell model, mass transfer is assumed to take place due to large eddies and small eddies, respectively. Then for the large eddy model of Fortescue and Pearson (1967), the mass transfer coefficient is given by

$$k_\ell = 1.46 \left(\frac{Du'}{\Lambda}\right)^{1/2} \qquad 2.27$$

where D is the molecular diffusivity of the species of interest in the liquid phase, u′ is the root mean square of the turbulent fluctuating velocity and Λ is the dimension of the roll cell. For the small eddy model of Lamont and Scott (1970), the mass transfer coefficient is given by

$$k_\ell = 0.4(D/\nu)^{1/2} (\varepsilon\nu)^{1/4} \qquad 2.28$$

where ν is the kinematic viscosity of the liquid phase and ε is the rate of turbulent energy dissipation. Both of these models should be applicable to characterize the uptake of atmospheric pollutants by water bodies if the parameters u′, Λ and ε can be obtained from turbulent velocity field measurements. In the more usual case when turbulence data are not available, ε can be obtained from a model of liquid phase behavior under wind shear as discussed by Kabel (1975). For this reason, the small eddy model was used in the overall air pollution model to determine the liquid phase mass transfer coefficient.

The use of the small eddy model depends upon the assumption of a logarithmic velocity profile in the liquid phase. While this might be considered to be done by an analogy to the gas phase, the physical pictures of momentum transport in the gas and liquid phases are really quite different

because of the differing boundary conditions. Nevertheless it does turn out (see Phillips, 1966; Shemdin, 1972), that a logarithmic velocity profile in a neutral liquid phase can be well documented. Such a profile then is described by the following equation.

$$u_w(0) - u_w(z) = \frac{w_*}{k} \ln\left(\frac{z}{z_{ow}}\right) \qquad 2.29$$

Parameters in this equation are the velocity in the water at the interface, $u_w(o)$, the velocity in the water at some depth, $u_w(z)$, the friction velocity in the liquid phase, w_*, von Karman's constant, k, the depth into the liquid phase, z, and the parameter, z_{ow}, which is the roughness height for the aqueous phase. Following Kraus (1972) we take the rate of turbulent dissipation of energy as

$$\varepsilon = -w_*^2 \frac{\partial u_w(z)}{\partial z} \qquad 2.30$$

If we differentiate the velocity profile equation to obtain the partial derivative of $u_w(z)$ with respect to z and substitute into Kraus's relationship, Equation 2.30, we obtain

$$\varepsilon = \frac{w_*^3}{k\, z} \qquad 2.31$$

The liquid phase friction velocity w_* is not well known and in order to apply this model we need to have some way of obtaining it. By the following reasoning we attempt to obtain it as a function of the friction velocity in the gas phase, which is much better characterized. We make the assumption of continuity of momentum flux across the interface; thus the shear stress in the air at the interface must be equal to the corresponding shear stress

in the water at the interface. The shear stress in the air is equal to $u_*^2\rho_a$, where ρ_a is the density of the air and the shear stress in the water correspondingly would be equal to $w_*^2\rho_w$, where ρ_w is the density of the water. This is written in equation form as

$$u_*^2\rho_a = \tau_{a_o} = \tau_{w_o} = w_*^2\rho_w \qquad 2.32$$

Thus we have a relationship between u_* and w_* through which we can eliminate w_* from Equation 2.31 for ε. The result is

$$\varepsilon = \frac{u_*^3}{k\,z}\left(\frac{\rho_a}{\rho_w}\right)^{3/2} \qquad 2.33$$

To obtain an effective value of the liquid phase mass transfer coefficient over the entire mass transport region, we need to take this $\varepsilon(z)$ and integrate it over the range to which the eddy mechanism applies. This range is from a, the depth of the molecular sublayer at the surface, to d, the depth of the mixed layer. Thus, the effective ε is given by the equation

$$\langle\varepsilon\rangle = \frac{1}{(d-a)}\int_a^d \varepsilon\, dz = \frac{u_*^3}{(d-a)k}\left(\frac{\rho_a}{\rho_w}\right)^{3/2} \ln\left(\frac{d}{a}\right) \qquad 2.34$$

When this effective rate of turbulent energy dissipation, $\langle\varepsilon\rangle$, is substituted into Lamont and Scott's Equation 2.28 for k_ℓ we obtain the following equation:

$$k_\ell = 0.4\left[\frac{D}{\nu}\right]^{1/2}\left[\frac{\nu u_*^3}{(d-a)k}\left(\frac{\rho_a}{\rho_w}\right)^{3/2}\ln\left(\frac{d}{a}\right)\right]^{1/4} \qquad 2.35$$

In this equation the molecular diffusivity of the pollutant, the kinematic viscosity of the water, and the densities of the air and water phases are all physical properties which should be known for any pollutant of interest. Again k is the von Karman constant, u_* is obtained from meteorological information, and d and a remain to be determined. The parameter, a, is the depth of the molecular sublayer, that region where eddy transport does not exist. This is commonly also called δ_w and can be obtained from a relationship given by Kraus (1972)

$$a = \delta_w = \frac{\nu \left(\frac{\rho_w}{\rho_a}\right)^{1/2}}{u_* k} \qquad 2.36$$

The depth of the mixed layer, d, is given by Phillips (1966) as

$$d = w_*/\Omega \sin\lambda \qquad 2.37$$

where Ω is the earth's angular velocity and λ is the latitude.

Equations 2.35, 2.36, and 2.37 now can be used to determine the liquid phase mass transfer coefficient. All of the physical quantities can be obtained. All that is required is the determination of u_* for the desired situation. This can be accomplished by using the following correlation presented by Hicks (1973) for the drag coefficient under neutral conditions:

$$C_{d_n} = (0.65 + 0.07\ u(10)) \times 10^{-3} \qquad 2.38$$

where C_{d_n} is the drag coefficient under neutral conditions when the under-

lying surface is water and u(10) is the mean wind velocity at a height of 10 metres above the underlying surface. Using the definition of shear stress at the surface, which is

$$\tau_{a_o} = \rho_a C_{d_n} u(10)^2 \qquad 2.39$$

and the definition of the friction velocity at the surface, which is

$$u_* = \sqrt{\tau_{a_o} / \rho_a} \qquad 2.40$$

together with Equation 2.38, one obtains the following relation

$$\frac{u_*^2}{u(10)^2} = (0.65 + 0.07\, u(10)) \times 10^{-3} \qquad 2.41$$

This relation relates the friction velocity at the surface to the wind-speed at a height of 10 metres.

Using the above methods, one can determine the Henry's Law constant, H, and the liquid phase mass transfer coefficient, k_ℓ, for the pollutant under consideration. With these quantities, the effect of the liquid phase on the process of pollutant transfer into water bodies can be quantified.

CHAPTER 3

APPLICATION OF THE THEORETICAL MODEL

INTRODUCTION

In this chapter the practical application of the theoretical model is discussed. This includes: 1) the development of point sources, 2) the determination of source heights, 3) developing a coordinate system, 4) mathematically defining the boundaries of the lakes for subsequent computer usage, 5) application of the model at the land-water interface where the vertical flux changes, 6) the method of calculating the flux into the lake, and 7) the quantification of the meteorological variables involved.

THE SOURCES

Each AQCR was modeled as a point source with an initial crosswind plume width equal to the diameter of a circle having an area equivalent to that of the AQCR. Every point source was modeled at a partially arbitrary height of 10 m. This decision was guided by 2 criteria:

1) the Pasquill-Gifford curves apply only to near ground-level sources,
2) the model required that H not be zero to prevent mathematically undefined statements.

The choice of 10 m as a small, non-zero height was thus made.

Modeling An Area Source As A Point Source

In actuality, each AQCR is an area source. As stated above, each area source was modeled as a point source with an initial crosswind spread. Therefore, the new crosswind dispersion parameter was written as follows:

$$\sigma_y' = (\sigma_{y_o}^2 + \sigma_y^2)^{1/2} \qquad 3.1$$

where

σ_y' = the new crosswind spread (m)

σ_{y_o} = the initial crosswind spread at the source (m)

σ_y = the crosswind spread as attained from the Pasquill-Gifford curves (m)

For convenience, σ_y' will be written as σ_y. It is this σ_y that was used in the previous equations of the theoretical development section.

There are two terms which are used in this report, the crosswind spread and the crosswind plume width. The first, the crosswind spread or crosswind dispersion parameter has been discussed. Since we have assumed the Gaussian distribution, it is probable that 68% of the plume mass lies within $\pm \sigma_y$ of the plume centerline and thus, σ_y is seen to be the standard deviation of the particle displacement from the centerline. The crosswind spread is thus a measure of dispersion. The second term, plume width, can be defined in terms of the plume spread as follows

$$w = 4.28\ \sigma_y \qquad 3.2$$

where w is the plume width. As a statistical parameter the distances of $\pm\ 2.14\ \sigma_y$ from the centerline define that point at which the concentration drops to 10% of the centerline value.

DEFINING A COORDINATE SYSTEM

Figure 3.1 depicts a fixed Cartesian coordinate system with an arbitrarily chosen origin overlaid on a map of the Great Lakes Basin and the surrounding AQCR (Acres, 1975). Grid points in the coordinate system are 53 km apart. The coordinates of each point source and of the lakes were recorded originally in this fixed system. Since the Gaussian model demands that the x direction be the downwind direction, measures were taken to easily transform the coordinate system from the original fixed system to whatever system was necessary to assure alignment of the x direction and the wind direction. Using the meteorological convention of depicting wind direction, i.e., 0° is from the north, 90° is from the east, etc., the following equations were developed:

$$x' = x \sin\theta - y \cos\theta \qquad 3.3$$

and

$$y' = x \cos\theta - y \sin\theta \qquad 3.4$$

where

x' = the new x coordinate

y' = the new y coordinate

x = the old x coordinate in the fixed system

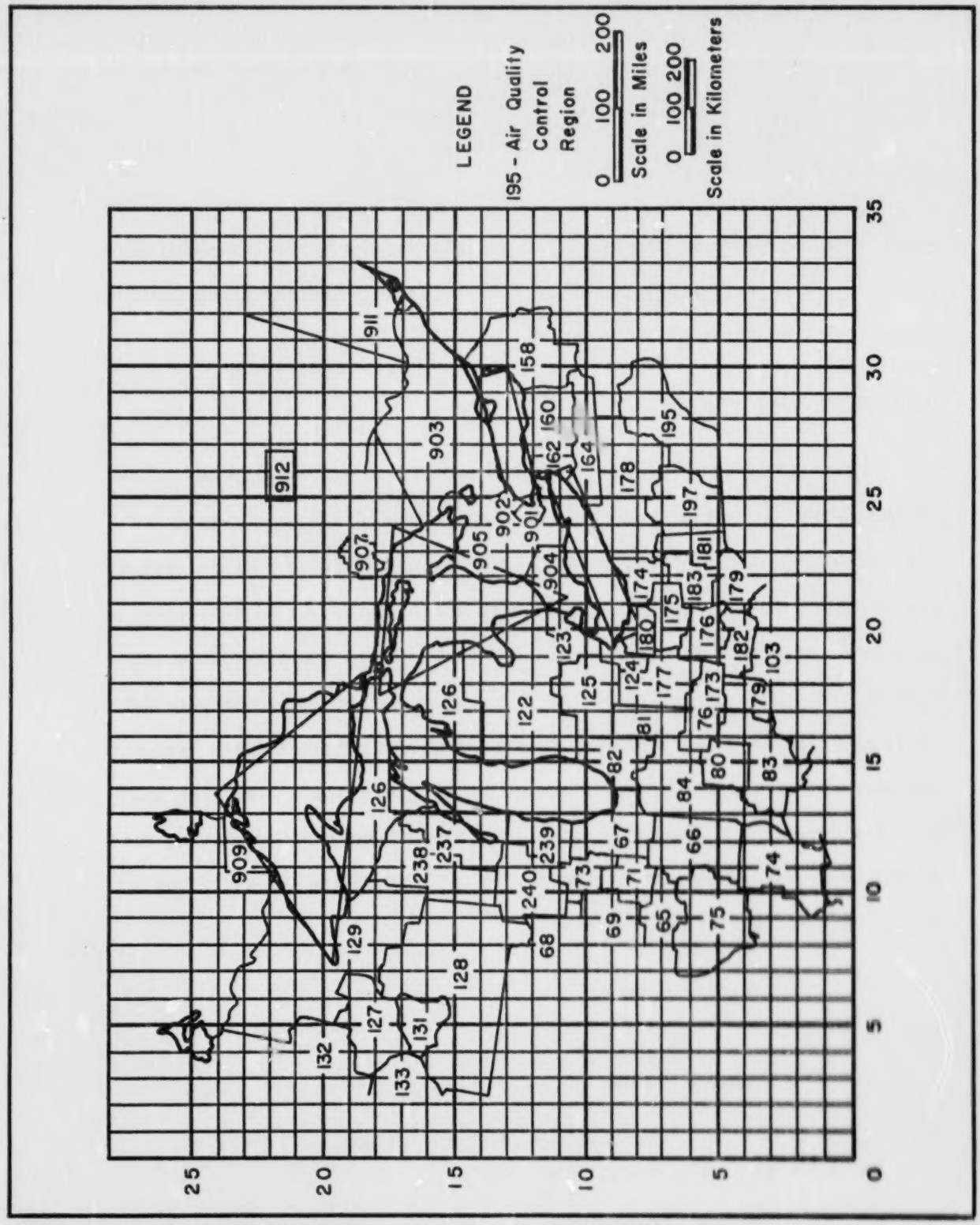

Figure 3.1: The Coordinate System and Lake Shape Simplifications

y = the old y coordinate in the fixed system

θ = the wind direction using the meteorological convention

Both the original coordinates of the point sources and their original plume widths and source strengths are listed in Table 3.1. The source strengths in Table 3.1 were acquired from the 1973 National Emissions Inventory as recorded in Acres (1975). This inventory was compiled using data from EPA National Emission Inventories, state files and provincial files in Canada. In the United States much of the basic data comes from State Implementation Plans for air pollution control submitted to the EPA.

MODELING THE LAKES

In order to simplify the model, the shapes of the 5 major lakes in the Great Lakes Basin were modeled as simple geometric figures as shown in Figure 3.1. Superior and Huron were modeled as triangles while Michigan, Erie, and Ontario were modeled as rectangles. This simplification was necessary since the computer must be programed to locate every point on the lake edge. Defining the lake edges by straight lines made this possible.

THE SUPERPOSITION OF PLUMES

The Gaussian model assumption is actually concerned only with individual plumes and states that the distribution of pollutants in a plume from a single point source is Gaussian in both the vertical and crosswind directions. Since the more complex model of this research deal with the estimation of concentrations at a receptor from several point sources, the method of superposition of plumes was utilized. The contribution at the receptor from every source individually was calculated and then all the contributions were summed to yield the net effect from the several sources.

TABLE 3.1: SOURCE LOCATION AND STRENGTH

AQCR	x-COORD	y-COORD	σ_{yo}(m)	NO_x Source Strength (Mg/YR)	Particulate Source Strength (Mg/YR)
65	8.6	7.0	31360	115000	205000
66	11.8	5.8	40120	54000	101000
*67A	12.0	9.8	21200	443000	221000
67B	11.8	8.4	21200	443000	221000
67C	13.2	8.0	21200	443000	221000
68	7.3	11.0	41200	33000	22000
69	8.5	8.8	40000	85000	52000
70	8.4	2.4	40000	434000	355000
71	10.4	8.3	19000	21000	42000
72	11.0	0.4	23200	278000	175000
73	10.7	10.1	23200	46000	33000
74	11.0	2.6	41200	39000	47000
75	8.8	5.2	47200	142000	120000
76	16.3	5.6	21200	39000	41000
77	13.7	0.9	40000	101000	107000
78	17.2	0.9	47200	60000	271000
79	17.3	3.4	31400	180000	259000
80	14.9	4.8	23200	.89000	78000
81	16.5	7.5	26800	36000	27000
82	15.1	8.8	32800	69000	72000
83	15.1	3.1	35400	95000	55000
84	13.8	5.9	44400	121000	133000
103	20.3	2.0	59000	139000	166000
122	17.6	12.5	62800	245000	196000
123	19.7	10.4	25000	2013000	378000
124	19.0	8.5	16400	118000	122000
125	17.5	9.9	34000	101000	52000

*Indicates AQCR has been subdivided.

TABLE 3.1: Continued

AQCR	x-COORD	y-COORD	σ_{yo}(m)	NO_x Source Strength (Mg/YR)	Particulate Source Strength (Mg/YR)
*126A	10.8	18.6	21600	5900	11000
126B	11.4	18.4	21600	5900	11000
126C	14.1	17.9	21600	5900	11000
126D	16.1	17.8	21600	5900	11000
126E	16.0	16.8	21600	5900	11000
126F	16.2	14.8	21600	5900	11000
126G	17.3	15.3	21600	5900	11000
126H	18.0	15.0	21600	5900	11000
127	4.9	18.1	40200	17000	15000
128	6.2	14.5	78600	90000	129000
*129A	9.0	21.8	23400	6300	11000
129B	7.2	22.1	23400	6300	11000
129C	5.3	22.6	23400	6300	11000
129D	6.0	20.8	23400	6300	11000
129E	7.5	20.5	23400	6300	11000
129F	6.0	19.7	23400	6300	11000
129G	7.8	18.6	23400	6300	11000
129H	9.3	18.4	23400	6300	11000
129I	6.8	18.0	23400	6300	11000
129J	9.4	17.0	23400	6300	11000
131	4.9	16.3	28400	166000	43000
133	1.8	16.2	52600	28000	43000
158	30.7	13.1	43400	103000	25000
160	27.9	11.4	31400	88000	31000
162	26.3	11.2	18600	90000	77000
164	27.1	10.0	31400	58000	24000
173	17.8	5.2	19000	82000	177000

*Indicates AQCR has been subdivided.

TABLE 3.1: Continued

AQCR	x-COORD	y-COORD	σ_{yo} (m)	NO_x Source Strength (Mg/YR)	Particulate Source Strength (Mg/YR)
174	22.0	7.9	23800	292000	359000
175	20.6	6.7	25000	34000	46000
176	19.7	5.4	16400	71000	100000
177	18.1	7.1	30000	63000	47000
178	25.4	8.4	49200	206000	321000
179	21.8	4.2	19000	102000	91000
*180A	19.3	7.9	12400	9500	45000
180B	20.5	7.5	12400	9500	45000
181	23.3	6.0	25000	178000	127000
182	19.5	4.3	25000	19000	58000
183	21.9	6.0	23200	62000	383000
195	27.8	6.8	46400	85000	203000
197	24.8	6.3	31400	415000	305000
*237A	12.3	15.0	21800	38000	39000
237B	11.8	14.5	21800	38000	39000
237C	12.7	13.5	21800	38000	39000
238	10.8	15.6	41200	77000	60000
239	12.1	11.6	29200	129000	140000
240	10.4	12.2	37800	31000	27000
**901	24.4	12.1	16400	110000	53000
902	24.7	12.9	16400	212000	43000
903	27.8	15.5	70800	12000	5000
904A	20.6	10.1	22200	72500	9000
904B	22.3	11.3	22200	72500	9000
905	23.4	13.0	49200	15000	20000
907	22.8	18.5	17400	5000	24000
908	18.3	18.7	9400	4000	57000
909	11.5	23.0	28400	5000	23000
912	25.8	21.7	16400	50000	11000

*Indicates AQCR has been subdivided.

**900's indicate Canadian AQCR

APPLICATION OF THE MODEL AT THE LAND-WATER BOUNDARY

The land-water boundary presents a point of discontinuity with respect to atmospheric stability. The difference in stability over water as compared to land is due in part to the difference in temperature between the water and land surfaces. Because of this discontinuity, a two step model was constructed.

The first step of the model consisted in applying the superposition of several Gaussian plumes expanding over a height limited by the land surface below and an inversion layer above. This part of the model was used to calculate the concentration at the upwind edge of the lake due to all the actual sources. Actually, a "wall" of concentrations was calculated at selected grid points as shown in Figure 3.2. The crosswind distance between grid points, Δy, was chosen as 50 km for reasons explained in the results section, and the vertical distance between grid points, Δz, was 200 m except in the lowest 200 m of the atmosphere over the lake in the summer when Δz = 20 m.

The second step of the model consisted of forming new source strengths, QN, at the upwind edge of the lake and, using these new source strengths along with the superposition of the resulting Gaussian plumes expanding over a height limited by the water surface and an inversion layer, calculating the flux into the lake from these sources. The new source strengths were acquired by averaging the concentrations at the four nodes of a grid and then multiplying by the flowrate of air through the grid:

$$QN_{i+1/2,\ j+1/2} = \frac{(C_{i,j} + C_{i+1,j} + C_{i,j+1} + C_{i+1,\ j+1})}{4} \cdot u \cdot \Delta y \cdot \Delta z \quad 3.5$$

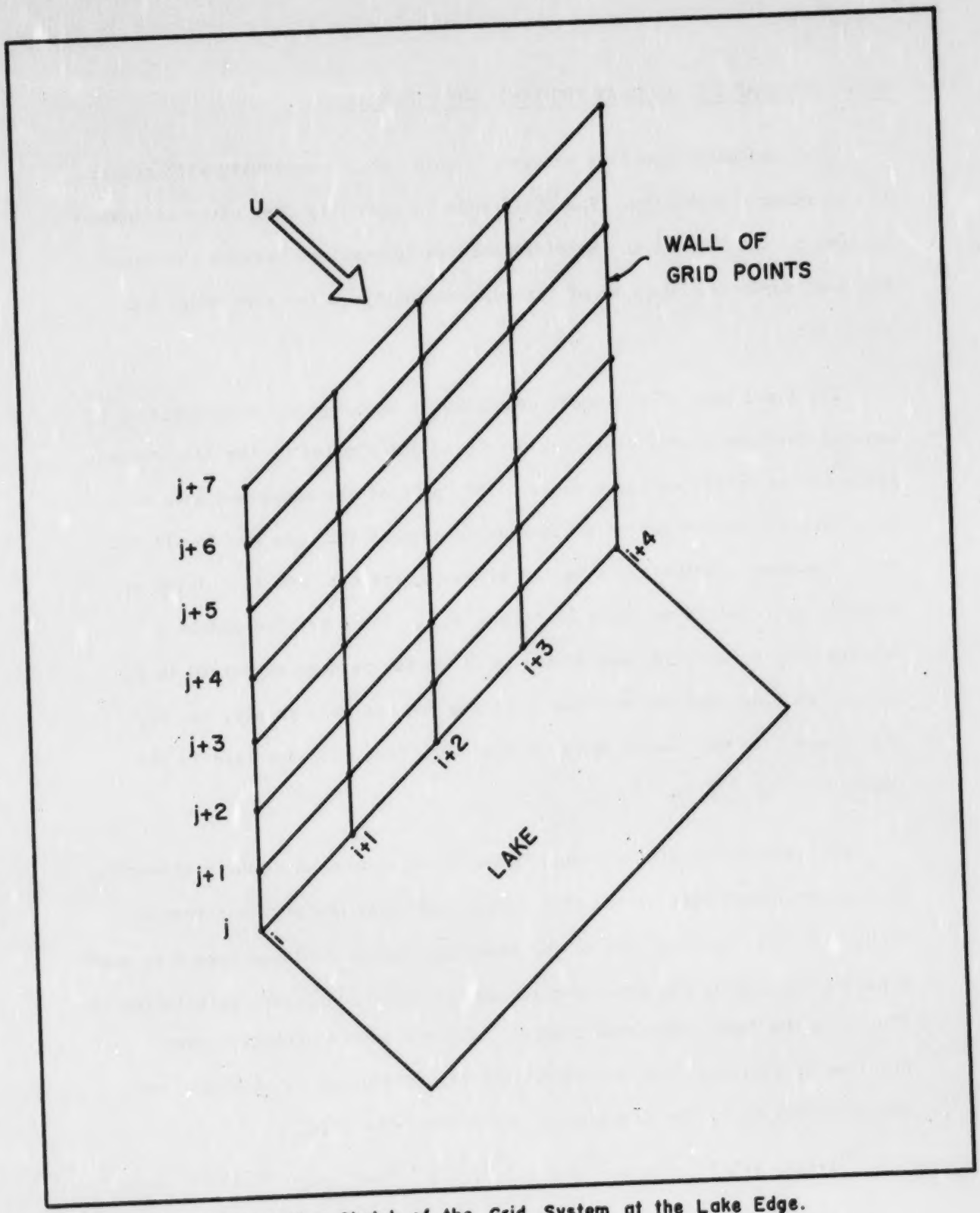

Figure 3.2: A Perspective Sketch of the Grid System at the Lake Edge.

The new point source of strength QN was then located in the center of the grid and given an initial crosswind plume width of Δy (where $\Delta y = 4.28\ \sigma_{yo}$) and an initial vertical plume width of Δz (where $\Delta z = 4.28\ \sigma_{zo}$).

When the case arose where pollutants were carried over one of the Lower Lakes before arriving at an Upper Lake the procedure was more complex. As in step one above, the concentration at the upwind edge of the first lake from the original sources was calculated. Step two consisted in forming new sources at the upwind edge and then using the model of the superposition of Gaussian plumes expanding over a height limited by the water surface and the inversion led to calculate the concentration at a second "wall" of grid points formed at the downwind edge of the first lake. Step three again began with the creation of still another set of new source strengths and concluded with the calculation of the concentration at a third "wall" of grid points at the upwind edge of the second lake. Finally, step four consists in forming a third set of new source strengths and using these to calculate the flux into the second lake which was an Upper Lake.

CALCULATING THE FLUX INTO THE LAKE

Using only the new sources formed on the upwind grid wall which were beneath the first inversion over the lake, the flux into the lake at several points was determined and then the average flux was calculated by summing the point fluxes and dividing by the number of points. It was assumed that the new sources above the inversion made no contribution to the input into the lake since their plumes did not penetrate the inversion lid. The coordinates of the 19 points on Lake Huron's surface and the 30 points on

Lake Superior's surface are given in Table 3.2. The average flux into the lake multiplied by the area of the lake ($5.95 \times 10^4 km^2$ for Huron and $8.23 \times 14^4 km^2$ for Superior) yielded the input rates into the lakes. This input multiplied by the amount of dry deposition time (determined as shown in the Meteorology section) yielded the yearly mass input into the two major Upper Great Lakes.

Confidence Level Of Model Estimates

We are indebted to Mr. Gerald F. Regan (EPA, Region V) for emphasizing that this report would be improved by some statement of confidence level of estimates provided by this model. It should be noted that the diffusion estimate for this model has required the estimation of parameters which are not well known. Ground level concentrations based on Gaussian models are considered to be valid within a factor of two to eight depending upon atmospheric stability and distance downwind. We have attempted to use realistic values considering the unique climatology of the Great Lakes including atmospheric conditions over the Lakes themselves.

The techniques for estimating dry deposition into the lakes were developed under this project. This is essentially a "new" model. Accuracy of these estimates can be no better than that of the Gaussian model for predicting atmospheric concentrations of pollutants. Despite this "order of magnitude" potential deviation of predicted from actual values (we do not feel the deviation is this large but many more samples must be collected to demonstrate this) the model does serve as a planning tool which can be used to predict the degree of pollution in the Upper Great Lakes resulting from airborne contaminants.

TABLE 3.2: LAKE COORDINATES AT WHICH FLUXES WERE DETERMINED

LAKE HURON

x-COORD	y-COORD
21.0	12.0
21.0	13.0
22.0	13.0
20.0	14.0
21.0	14.0
22.0	14.0
20.0	15.0
21.0	15.0
22.0	15.0
19.0	16.0
20.0	16.0
21.0	16.0
22.6	16.0
23.0	16.0
19.0	17.0
20.0	17.0
21.0	17.0
22.0	17.0
23.0	17.0

LAKE SUPERIOR

x-COORD	y-COORD
8.0	20.0
9.0	20.0
10.0	20.0
11.0	20.0
12.0	20.0
13.0	20.0
14.0	20.0
15.0	20.0
16.0	20.0
17.0	20.0
13.0	19.0
14.0	19.0
15.0	19.0
16.0	19.0
17.0	19.0
9.0	21.0
10.0	21.0
11.0	21.0
12.0	21.0
13.0	21.0
14.0	21.0
15.0	21.0
16.0	21.0
11.0	22.0
12.0	22.0
13.0	22.0
14.0	22.0
15.0	22.0
13.0	23.0
14.0	23.0

CHAPTER 4

DATA, POSTULATES & INPUT PARAMETERS

METEOROLOGY

The Pasquill-Gifford Curves

The Pasquill-Gifford Curves (Turner, 1970) were fitted according to the following equation (Lawrence, 1971):

$$Y = 10^{(A_0 + A_1 \log x + A_2(\log x)^2 + A_3 (\log x)^3)} \qquad 4.1$$

where

Y = the horizontal or vertical dispersion parameter (m)

x = downwind distance (m)

A_0 - A_3 = coefficients best defining the Pasquill-Gifford curves.

Table 4.1presents Lawrence's determination of the coefficients for the stability classes defined by Pasquill where A is a highly unstable and dispersive atmosphere and F is very stable and non-dispersive.

The Pasquill-Gifford curves were originally plotted for a range of downwind distances from .1 to 100 km. It has been stated (Turner, 1970) that the accuracy of these curves decreases dramatically as one moves farther downwind with no greater accuracy than a factor of 2 claimed at

TABLE 4.1: VALUES OF THE COEFFICIENTS OF THE POLYNOMIALS DESCRIBING PASQUILL'S AND GIFFORD'S ATMOSPHERIC DISPERSION CURVES (Lawrence, 1971)

$$[Y = 10^{(A_0 + A_1 \log x + A_2 (\log x)^2 + A_3 (\log x)^3)}]$$

where x and Y are in metres

Stability Category	Y=	A_0	A_1	A_2	A_3
A	σ_y	- 0.25107	+ 0.86045	0.0	0.0
	σ_z	+15.074	-16.138	+5.9015	-0.63405
B	σ_y	- 0.91606	+ 1.1497	-0.037606	0.0
	σ_z	- 1.2415	+ 1.0935	0.0	0.0
C	σ_y	- 0.97311	+ 1.0685	-0.023721	0.0
	σ_z	- 1.1571	+ 1.0252	-0.015059	0.0
D	σ_y	- 1.2847	+ 1.1405	-0.033376	0.0
	σ_z	- 1.8630	+ 1.7337	-0.26787	+0.021036
E	σ_y	+12.218	-10.858	+3.4263	-0.32572
	σ_z	- 4.2034	+ 3.5279	-0.74226	+0.06037
F	σ_y	+15.433	-13.805	+4.2653	-0.40344
	σ_z	- 1.8971	+ 1.3812	-0.12244	0.0

distances over 100 km. The large distances concerned with in this research effort demanded that the curves be extrapolated beyond the 100 km limit since dispersion parameters at distances up to 800 km were required. This extrapolation was performed with recognition that the errors incurred in the quantification of the dispersion coefficients were at the very least a factor of 2. Other limitations of the Pasquill-Gifford curves which are important are:

1) They apply for a roughness length, $z_o \sim 3cm$

2) The σ_y curves apply only for short sampling time $T_s \sim$ 2-6 minutes

and

3) They apply only for ground level sources.

The Seasonal Variation Of Mixing Depth And Stability

An average mixing depth of 2000 m was assumed to extend over the land during all seasons of the year. The 2000 m average mixing depth was chosen after consideration of the changes in mixing depth with season, with synoptic meteorological conditions and the depth of the atmosphere through which large scale flow patterns are affected by the presence of the Great Lakes (Moroz, 1967, 1968, Koczkur et al. 1970). The model could be refined by using Holzworth's mixing depths (Holzworth, 1972), over land, upstream from the lakes at some penalty in computer time but use of these mixing depths downstream from the lakes would be incorrect: (Petterssen & Calabrese, 1949). Since 2000 m value incorporated mixing as a result of air passage over the Lower Great Lakes for some wind directions, and since the model appeared to be relatively insensitive to small changes in mixing depths, the 2000 m average mixing depth was consistently applied.

The 2000 m mixing depth was regarded as the first inversion over water during all seasons of the year except the summer during which the cold water and the warm overlying air create a surface inversion layer assumed to extend up to 200 m over the water. Thus, during the summer, the 2000 m mixing depth was regarded as the second inversion over water. Table 4.2 shows the seasonal variation of mixing depths and stability.

The stability over land and water is assumed to be the same in every season but the summer when the water surface is cooler than the land surface causing a more stable atmosphere over the water than over the land. The variation of stability over land with seasonal change shows a tendency toward a less stable atmosphere as one moves from spring through winter.

TABLE 4.2: SEASONAL VARIATION OF MIXING DEPTH AND STABILITY

Season	Stability Over Land	Stability Over Water	Height of First Inversion (m)	Height of Second Inversion (m)
Spring	E	E	2000	-
Summer	D	F	200	2000
Fall	D	D	2000	-
Winter	D	D	2000	-

This is due to the fact that in the spring the ground is still cold while the air above is warm causing an increasing temperature with height and a consequently more stable atmosphere in the spring. In the summer the ground is warm and the overlying air is warm so that conditions are less stable than in the spring. In the fall the ground is still warm while the air is cooler than in the summer and again one finds less stable conditions than in the spring. Finally, in the winter the ground is cold and air is cold again providing a less stable situation than the spring.

The Available Meteorological Data

The meteorological data used was taken from 14 stations in the Great Lakes vicinity as shown in Figure 4.1. All 14 stations yielded the daily averaged wind speed and direction, and the amount and type of precipitation. Ten of the 14 stations also yielded the number of hours of precipitation on a daily basis. These daily data were available for the entire year of 1973.

Determination of the Dry Deposition Time

The number of dry hours per year was determined in the following manner. If any station indicated precipitation for more than 12 hours, the entire 24 hour day was labeled a wet day and subtracted from the total monthly hours. This was simply a maneuver to reduce the great volume of data that were manipulated. This reduced monthly total was further diminished by subtracting all the hours of precipitation during the month considering only days with less than 12 hours of precipitation. This final total was the total monthly dry hours. Then the percent of time during a month that the

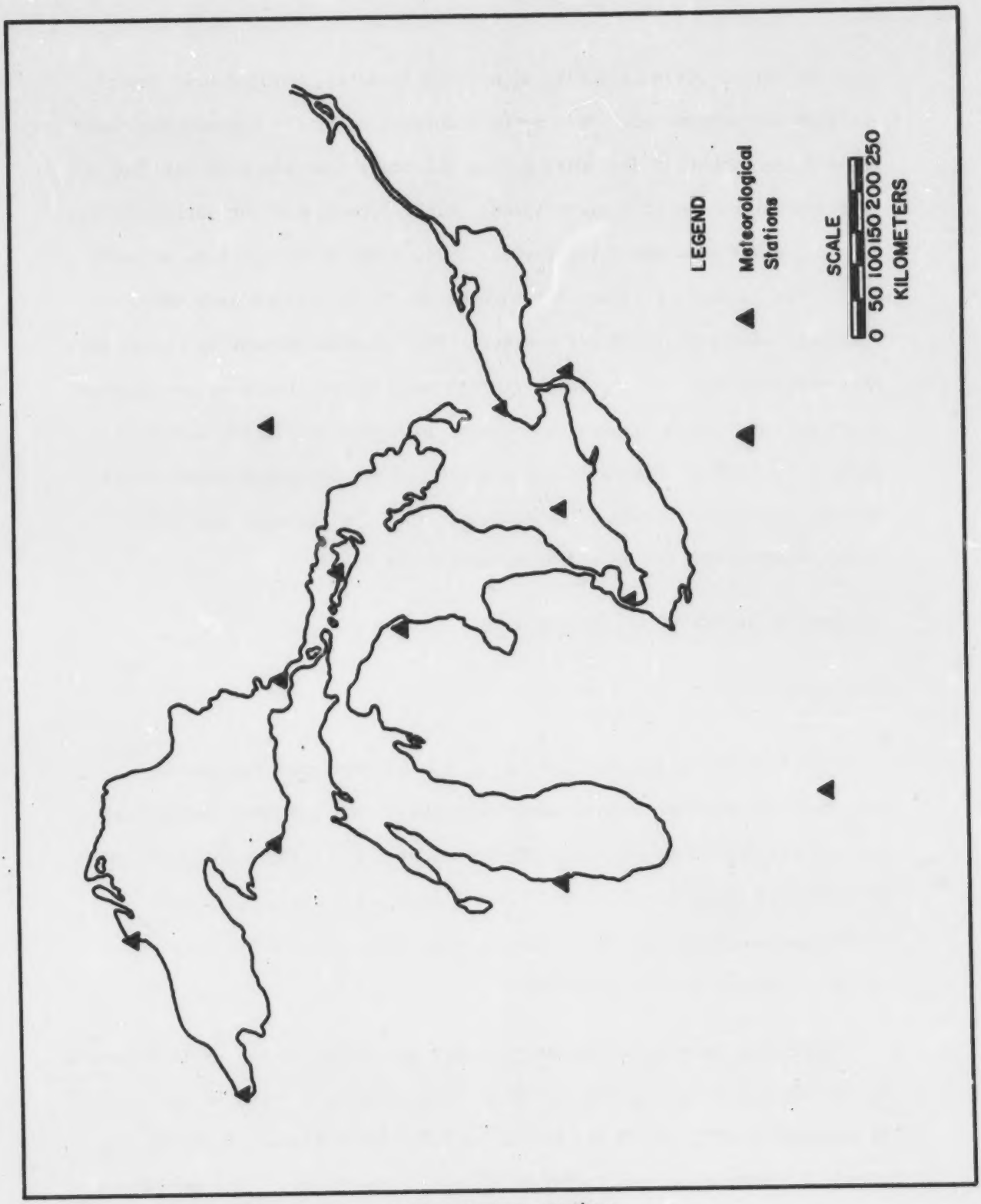

Figure 4.1: Upper Great Lakes — Meteorological Stations

wind was from a given direction at a given speed as averaged over the 14 stations was determined. This percent multiplied by the dry monthly hours yielded the number of dry hours during the month that the wind was from a given direction and at a given speed. Eight directional categories, N, NE, E, etc., and 4 wind speed categories; 2.24, 4.48, 6.72, and 8.96 m/s were used. The 12 monthly values for each of the 32 categories were added to yield the yearly hours of dry weather. The addition of monthly values on a seasonal instead of yearly basis yielded the seasonal hours of dry weather. Since only data from January to December 1973 were available, winter was defined as January, February, and December 1973. The other seasons were divided normally. Tables 4.3 through 4.7 show the seasonal and yearly yield of dry hours for each wind direction and speed.

DETERMINING TRANSPORT VALUES FOR GASES

Determination Of k_ℓ And H for NO_2

The theoretical model to determine k_ℓ was developed for gaseous pollutants in general. While the liquid phase mass transfer coefficient for any gas could be obtained using Equations 2.32, 2.35, 2.36, 2.37, and 2.41, k_ℓ was actually calculated for NO_2 only since other gases were eliminated as important for various reasons considered in the section entitled Species Characterization.

Examining Equation 2.35, the physical quantities necessary to determine k_ℓ for NO_2 are D, ρ_a, ρ_w and ν. These quantities were found in the literature at 25°C and 98.066 kPa to be 2.6×10^{-5} cm^2/sec, 0.001185 g/cm^3, 0.999044 g/cm^3 and 0.008946 cm^2/sec, respectively. The parameters

TABLE 4.3: TOTAL DRY HOURS BY WIND SPEED AND DIRECTION FOR THE ENTIRE YEAR 1973

	2.24 m/s	4.48 m/s	6.72 m/s	8.96 m/s
NW	136	249	114	42
N	244	418	129	26
NE	125	185	39	8
E	589	523	55	13
SE	141	109	28	7
S	472	479	89	30
SW	297	417	164	83
W	575	800	270	102

TABLE 4.4 TOTAL DRY HOURS BY SPEED AND DIRECTION FOR WINTER, 1973

	2.24 m/s	4.48 m/s	6.72 m/s	8.96 m/s
NW	27	46	32	8
N	58	131	51	14
NE	25	40	16	3
E	119	131	23	3
SE	21	15	7	4
S	66	73	33	10
SW	53	113	66	29
W	148	174	92	32

TABLE 4.5: TOTAL DRY HOURS BY WIND SPEED AND DIRECTION FOR SPRING, 1973

	2.24 m/s	4.48 m/s	6.72 m/s	8.96 m/s
NW	31	67	37	22
N	58	133	55	12
NE	28	82	20	5
E	166	205	26	10
SE	30	38	9	-
S	80	95	24	10
SW	37	61	30	10
W	71	172	65	16

TABLE 4.6: TOTAL DRY HOURS BY WIND SPEED AND DIRECTION FOR SUMMER, 1973

	2.24 m/s	4.48 m/s	6.72 m/s	8.96 m/s
NW	40	55	17	2
N	59	86	12	-
NE	36	40	-	-
E	170	72	4	-
SE	37	30	7	-
S	192	184	13	4
SW	146	153	39	27
W	198	214	19	3

TABLE 4.7 : TOTAL DRY HOURS BY WIND SPEED AND DIRECTION FOR FALL, 1973

	2.24 m/s	4.48 m/s	6.72 m/s	8.96 m/s
NW	38	81	28	10
N	69	68	11	-
NE	36	23	3	-
E	134	115	-	-
SE	53	26	5	3
S	134	127	19	6
SW	61	90	29	17
W	158	240	94	51

required to determine k_ℓ are a, d and u_*. The friction velocity, u_*, was obtained from Equation 2.41 for various wind speeds. Then the depth of the molecular sublayer, a, was obtained from Equation 2.36 with k taken equal to 0.4. Finally, the depth of the mixed layer, d, was calculated using Equation 2.37 with Ω taken equal to 1.46×10^{-4} sin λ and λ taken to be 45°. In Equation 2.37, the liquid phase friction velocity, w_*, was determined from Equation 2.32. In the model, wind speeds of 2.24, 4.48, 6.72, and 8.96 m/s were used. The results for the friction velocity, u_*, and the liquid phase mass transfer coefficient, k_ℓ, for each wind speed are presented in Table 4.8 for the system nitrogen dioxide - water at 25°C and 98 kPa total pressure.

TABLE 4.8: Determination of k_ℓ for the system NO_2 - H_2O.

u(10), m/s	u_*, cm/sec	$k_\ell \times 10^3$, cm/sec
2.24	6.36	0.69
4.48	13.90	1.07
6.72	22.50	1.39
8.96	31.90	1.68

The determination of the solubility of a species in a liquid phase is fairly simple in most cases. However, in the case of nitrogen dioxide, which reacts with the aqueous phase forming a variety of ionic species, this determination becomes very complicated as indicated by Kabel (1975). Also, very little data are available for the absorption of NO_2 in water. However, a study performed by Wendel and Pigford (1958) yields some useful

information. Using experimental results combined with thermodynamics, Wendell and Pigford obtained the following result for Henry's Law constant for the system nitrogen dioxide - water at 25°C and 98 kPa total pressure:

$$H = \frac{C_{gi}}{C_{\ell i}} = 4.3 \times 10^{-2} \quad \frac{g/cm^3 \text{ gas}}{g/cm^3 \text{ liquid}}$$

Determination Of The Deposition Velocity Over Land For NO_2

The deposition velocity over land was determined by observing its counterpart over water, i.e. k_ℓ/H. For NO_2, k_ℓ/H as determined from Table 4.8 has values ranging from .00016 m/s to .0004 m/s. Since the uptake over land should be less than the uptake over water, all variables but the deposition rate considered equal, a value of .0001 m/s was arbitrarily selected below the range of k_ℓ/H values for the deposition velocity of NO_2 over land.

DETERMINATION OF PARTICULATE TRANSPORT VALUES

Determination Of The Particulate Deposition Velocity In The Atmosphere

Atmospheric particulate matter is characterized by an entire range of sizes. Each particle size settles at its own individual velocity dependent on gravitational forces and drag forces, turbulent eddy diffusion and molecular diffusion. It is often assumed that the deposition velocity is equivalent to the Stokes fall velocity, V_s, which only considers gravitational and drag forces. This is satisfactory for a still atmosphere and for particles large enough to allow the atmosphere to be viewed as a continuum but for a turbulent situation or for particle sizes on the order of

the mean free distance between air molecules, the actual deposition velocity is larger than the Stokes settling velocity. This increase in deposition velocity (V_d) over the Stokes settling velocity (V_s) is shown in Figure 4.2.

The Quasi-Polydispersoid Particulate Model

The particles emitted from the various sources were assumed to be amenable to representation as a log-normal size distribution. The mass mean diameter was chosen as 0.76μm with a geometric standard deviation of 5.0. The mass mean diameter was an average of one day samples taken randomly over the year 1970 in the city of Chicago with measurements being made by a modified Andersen Cascade Impactor (Lee, 1972).

With the size distribution defined, 3 size categories containing equal mass were determined. The three ranges such that each contained 33% of the mass were: .01-.33μm, .33-1.5μm, and 1.5-40μm. Using Figure 4.2 (Sehmel, 1975), an average deposition velocity was selected for each size range with consideration given to the effect of surface roughness, atmospheric stability, friction velocity, particle density, and the height at which the deposition velocity was being estimated. Particles from .01-.33μm were estimated to have an average fall velocity of .011 m/s; particles from .33-1.5μm were estimated to fall at .006 m/s, and particles from 1.5-40μm were estimated to fall at .019 m/s. Note that the velocity in the smallest category is larger than the velocity in the intermediate size range. This is due to the increased molecular diffusion of the smallest range. In using Figure 4.2, the average particle density was assumed to be 4 g/cm^3; a stable atmosphere was assumed, a roughness length

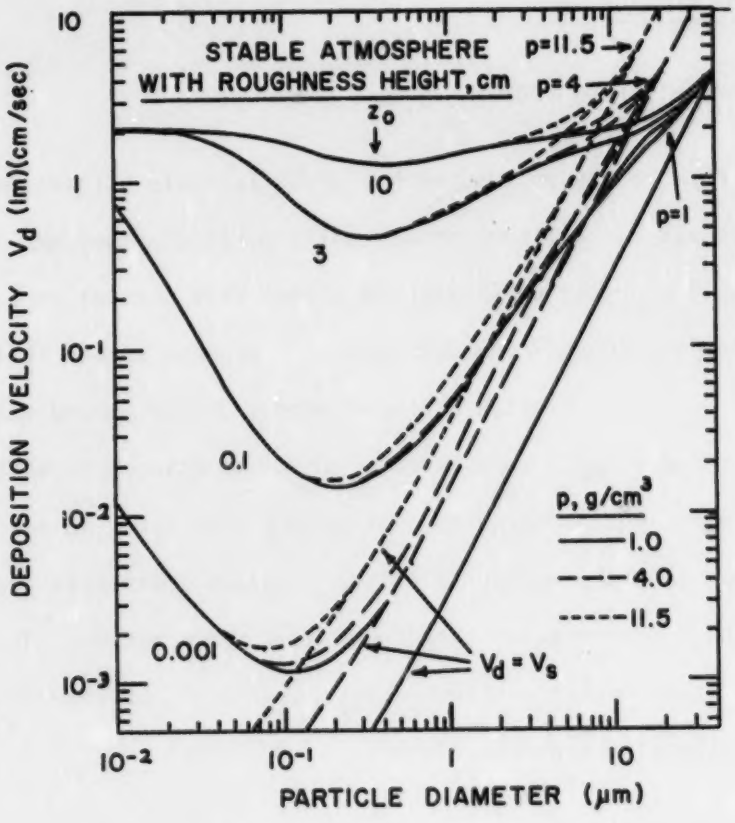

Figure 4.2: Predicted Deposition Velocities at 1 Metre for $u_* = 30$ cm/sec and Particle Densities of 1, 4, and 11.5 g/cm³ (Sehmel, 1975).

of 3 cm was selected, a friction velocity of 30 cm/s was chosen and a depth of 1 m above the ground was the depth over which the deposition velocities were averaged.

BACKGROUND CONCENTRATIONS

Background Concentrations For NO_2

The source strength values for NO_2 given in Table 3.1 accounted for industrial processes, fuel combustion, solid waste disposal and transportation processes but neglected background values from natural processes. An analysis of the air composition for Duluth, Minnesota showed that the minimum daily NO_x concentration measured over a 5 year period with samples taken biweekly was 3 $\mu g/m^3$ (HEW, 1962). This was assumed to have occurred on a day when most sources were inoperative and when the wind was from the NW bringing air from the unindustrialized Canadian grasslands and was chosen as a quite conservative background NO_2 concentration. Other reports have indicated that background concentrations for NO_2 of 2.0-2.5 $\mu g/m^3$ are reasonable estimates (Rasmussen, Taheri, Kabel, 1974).

Background Concentration For Particulate

As in the case of NO_2 gas, the AQCR source strengths did not include particulate from fugitive dust sources such as vehicular travel on paved and unpaved surfaces, agricultural activities, and wind erosion of soil to mention a few. Again looking at Duluth as a representative city in the Upper Great Lakes Region, the minimum particulate concentration measured over the 5 year period from 1957-1961 was 19 $\mu g/m^3$ for a 24 hour average.

Again assuming that this occurred on a day when most sources were inoperative and when the wind was from the unindustrialized Canadian grasslands NW of Duluth, the value of 19 $\mu g/m^3$ was chosen to represent the background concentration.

CHAPTER 5

SPECIES CHARACTERIZATION

POLLUTANTS NOT CONSIDERED IN THE MODEL

Elimination Of Nitrous Oxide And Nitric Oxide As Detrimental To The Upper Great Lakes

Gaseous nitrous oxide, although being the most abundant nitrogen compound in the atmosphere, was not considered a detrimental pollutant to the Upper Great Lakes. Nitrous oxide is produced naturally from bacterial decomposition of other nitrogen compounds within the soil; however, there are very few data available to quantify these natural emissions. More importantly, nitrous oxide is almost insoluble in water and could not contribute significantly to the nitrogen budget of the Great Lakes.

Gaseous nitric oxide is emitted from anthropogenic and natural sources. Generally, estimates of emissions for NO and NO_2 are included together as NO_x such as in the National Emissions Inventory data listed in Table 3.1. NO readily oxidizes to NO_2 and since this research deals with long range transport, the oxidation was thought to be so complete that the emissions data for NO_x could be considered to be completely NO_2. Therefore, due to this oxidation process and, in addition, to the low solubility of NO in water, NO was not considered to contribute significantly to the nitrogen budget of the Great Lakes.

Elimination of Ammonia From Model Considerations

Ammonia was not included in the model in either gaseous or particulate form even though there is a significant gaseous input into the atmosphere each year from predominantly natural sources (Rasmussen, Taheri, Kabel, 1974). The reason for neglecting NH_3 is not because there is a dearth of emissions nor because NH_3 is not soluble in water. This predominantly natural emission was omitted due to a lack of emissions data. It is thought that ammonia could have a significant impact on the nitrogen budget of the Great Lakes.

INDIVIDUAL POLLUTANT CONTRIBUTIONS TO THE UPPER GREAT LAKES

Total Dissolved Solids

The percent of the total particulate input into the Upper Great Lakes that is water soluble was estimated by considering dustfall bucket measurements taken in the Greater Windsor Area from 1951-1955 (Katz, 1961). The water soluble fraction was calculated and found to vary from 20 to 30%. The lowest value of 20% was selected for this application to allow for the reduction in readily dissolved sulfate emissions caused by the shift from coal to oil and gas during the 1951-1973 period. With the tendency to shift back to coal in this era due to energy considerations, the water soluble percentage may again increase.

Chlorides

The percent of the total particulate input into the Great Lakes that was chlorides was assumed to be equivalent to the percent of the total particulate emitted from all the sources in the Great Lakes Region that was chlorides. This latter percentage was calculated by Acres (1975) to be .52%. It was also assumed that this percent represented the ratio of the average chloride concentration to the total particulate concentration, so that the

average chloride concentration was calculated as .52 $\mu g/m^3$ using the National Air Sampling Network (NASN) measurement of 104 $\mu g/m^3$ as representative of the total yearly particulate concentration (HEW, 1962). Katz (1961) indicated that the maximum particulate chloride concentration measured by NASN during an 18 month sampling period was 7.6 $\mu g/m^3$ for a 24 hour period.

Katz also reported data from which it was determined that the average urban concentration of gaseous chloride for a highly industrialized area was .075 PPM by volume or 119 $\mu g/m^3$. Thus the concentration of gas is, on the average, 200 times as great as solids with differences as small as a factor of 15 occurring over occasional short periods.

This large gaseous chloride input was an unexpected development discovered late in the project. Because of the time element, the gaseous chloride input was calculated simply as a factor of 200 times the particulate chloride input. Were more time available, the gaseous chloride input could have been better determined by multiplying each particulate source by .0052 x 200 and using these gaseous chloride source strengths and the k_ℓ, H and V_d for gaseous chlorides to determine the input into the lake.

Total Nitrogen

The gaseous contribution to the total nitrogen budget of the Upper Great Lakes was determined using the given AQCR source strengths, the given meteorological data and the predictive model. The gaseous input consists only of NO_2.

The particulate contribution to the nitrogen budget was simply computed as a given percentage of the total particulate input. NASN measurements produced a five year geometric mean concentration for particulate nitrates of 1.7 $\mu g/m^3$. Since the total suspended particulate geometric mean for the same period was 104 $\mu g/m^3$, 1.6% of the particulate in the air, and consequently, 1.6% of the total particulate input into the Upper Great Lakes was estimated as particulate nitrates.

Total Phosphorus

The total phosphorus input was calculated solely as particulate since there was no information available identifying any form of gaseous phosphorus or gaseous phosphorus containing atmospheric pollutants either for natural or anthropogenic sources.

The particulate phosphate input was calculated as a percent of the total particulate input. Acres (1975) calculated that .0115 grams of phosphate were in every gram of particulate emitted from sources in the vicinity of the Great Lakes. Given that 1.15% of the particulate emitted was phosphates, it follows that 1.15% of the total particulate input into the Upper Great Lakes was particulate phosphate. The assumption depends on a further assumption that the size distribution of the particulate phosphate was similar to the size distribution of the total particulate.

Dissolved Silica

The total silica input into the Great Lakes was calculated as a percent of the total particulate input. Cholak (1952) has measured the silica in the air in Baltimore as 3.5% of the total particulate. Katz (1954) found

that the mean (averaged over 23 samples) concentration of silica in the Windsor area was 6.2 $\mu g/m^3$ (expressed as elemental silicon) while the mean total particulate concentration was 196 $\mu g/m^3$. Therefore, 3.2% of the total particulate was elemental silicon which would correspond to about 7% silica. Unfortunately, what could not be estimated was the dissolvable portion. Ultimately, Cholak's value of 3.5% was used. Thus 3.5% of the total particulate input was silica and it is the total silica and not the dissolved silica that is reported in the Results section.

Pesticides

The Source Strengths

The emission factors for pesticides originated from data showing the amount of pesticides, that is, fungicides, herbicides, insecticides and miscellaneous fumigants, defoliants, miticides, rodenticides, plant growth regulators, and repellents used in the year 1971 (USDA, 1974). These data were given on a regional basis with the three regions of importance being the Lake States: Minnesota, Wisconsin, and Michigan, the Corn Belt States: Iowa, Illinois, Indiana, and Ohio, and the Northeast States of which only New York and Pennsylvania were in the Great Lakes Basin. Since only one number was given for the pesticides emissions from a region, the decision was made to determine the pesticides utilized in each state in the Great Lakes Basin by modifying the regional value by multiplying it by the percentage of the region's farmland contained in each state. Thus, if a state contained 50% of the farmland of its region, it was assumed to use 50% of the region's pesticides. In this fashion, nine source strengths were attained, each source representing an entire state. Each state was modeled

as a point source located in the middle of the state with an initial crosswind plume width equal to the diameter of a circle with an area equivalent to the total area of the state. The values of the weighted source strength and the weighting factor used, along with the initial crosswind diffusion coefficient are shown in Table 5.1.

Pesticides In Particulate Form

It was estimated that 50% of the applied pesticides did not settle on the farmlands but rather, were dispersed into the atmosphere (Westlake and Gunther, 1966). The pesticide particle remaining after the solvent in which it was originally dispersed evaporated was assumed to be in the third size category, 1.5 to 40 μm. Thus, the average pesticide particle's deposition velocity was estimated as .019 m/s. Given the deposition velocity, the initial source strengths and locations, the initial plume widths and the meteorological data, the mathematical model was used to determine the input of pesticides into the Upper Great Lakes. No background concentration was utilized for pesticides.

TABLE 5.1 : EMISSION FACTORS FOR PESTICIDES

Region	Airborne Factor	Weight Factor	Total Regional Pesticides (Mg/YR.)	Weighted Emission Factor (Mg/YR.)	σ_{yo} (m)
LAKE STATES			16026.		
Minnesota	.5	.466		3734.	131603.
Wisconsin	.5	.308		2468.	107557.
Michigan	.5	.226		1810.	109514.
CORN BELT			45606.		
Iowa	.5	.258		5883.	107687.
Illinois	.5	.221		5039.	107793.
Indiana	.5	.137		3124.	86467.
Ohio	.5	.135		3078.	92154.
NORTHEAST			9461.		
Pennsylvania	.5	.288		1362.	96640.
New York	.5	.341		1613.	101066.

CHAPTER 6

RESULTS

The results presented in this report are only estimates. Some portions of the quantitative modeling are familiar and well defined whereas other aspects rely heavily on intuition. This section shows the effects on the input into the lake of variation in some of the quantitative estimates of the input values. Also shown is a sample of the computer output depicting concentration and flux at a point on the lake edge. Finally, a compilation of results which shows the input of pollutants into the Upper Great Lakes is given.

A PARAMETRIC STUDY

The question to be considered in this section is how sensitive the model is to variation in the input parameters, specifically, original source height, grid dimension at the lake edge, inclusion of a background concentration, inclusion of an inversion lid over land, and variation in deposition velocity over land. Table 6.1 shows the results of varying these input parameters for the specific case of NO_2 dispersion with D stability over land and a first inversion of 200 m over water with the wind at 8.96 m/s from the SW.

TABLE 6.1 : VARIATION OF INPUT RATE OF NO_2 INTO THE UPPER GREAT LAKES AS A FUNCTION OF MODEL INPUT PARAMETERS

	COMPUTER RUN NUMBER										
MODEL INPUTS*	1	2	3	4	5	6	7	8	9	10	11
SOURCE HEIGHT (m)	1.0	1.0	1.0	1.0	1.0	10.	1.0	10.	10.	1.0	10.
DEPOSITION VELOCITY (mm/s)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	1.0	0.1
BACKGROUND CONCENTRATION ($\mu g/m^3$)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	0.0	0.0	3.0	3.0
INVERSION LID HEIGHT OVER LAND (km)	2.0	2.0	2.0	2.0	**	**	**	**	**	2.0	2.0
STABILITY CLASS OVER WATER	F	F	F	F	F	F	F	F	D	F	F
CROSSWIND GRID DIMENSION (km)	50.	25.	12.	6.2	50.	50.	20.	50.	50.	50.	50.
MODEL OUTPUTS											
INPUT RATE FOR LAKE SUPERIOR (kg/s)	.34	.42	.29	-	.34	.34	-	.13	.01	.21	.30
INPUT RATE FOR LAKE HURON (kg/s)	1.3	1.8	1.3	1.2	1.2	1.2	.68	1.1	.23	.21	.87

* Stability class over land was D and inversion lid over water was at 200m for all runs. This parametric study yields input rates utilizing only sources SW of the Upper Great Lakes.

** No lid existed.

Variation Of Results With Grid Size

In the finite difference approximation of the diffusion equation for computer solution, there is a direct relation between the increase in accuracy achieved by using a finer grid network and the increased cost for computer time incurred. Also, there exists a point where no finer grid can be used due to the limitation of storage space in the computer. While the model used in this research was not a partial differential equation, a grid network was used at the lake edge and the above concepts were thought to apply.

The variation of input rate with the crosswind grid dimension can be seen by inspecting run numbers 1 through 4 in Table 6.1 . The variation is more clearly depicted in Figure 6.1 where the variation in lake input is plotted as a function of the crosswind distance between grid points. The plot stops at 6 km because any computer run with $\Delta y<6$km was bound to exceed the storage limit of 560K bits. (The actual storage limit when using the Pennsylvania State University IBM Model 370 System is 280K. The 560K storage requires special permission which is only given for debugging purposes. Thus the 560K storage is not available for continuous use.) The slopes in Figure 6.1 showed signs of decreasing to zero as Δy decreased but it was not possible to confirm this fact due to storage limitations. Fortuitously, the variation with grid size was not pronounced and the flux values obtained at $\Delta y=50$km were near those obtained at $\Delta y=6$km. Therefore, in order to minimize computer usuage in terms of time, storage and consequently, cost, the grid size of $\Delta y=50$km was used in all the predictions.

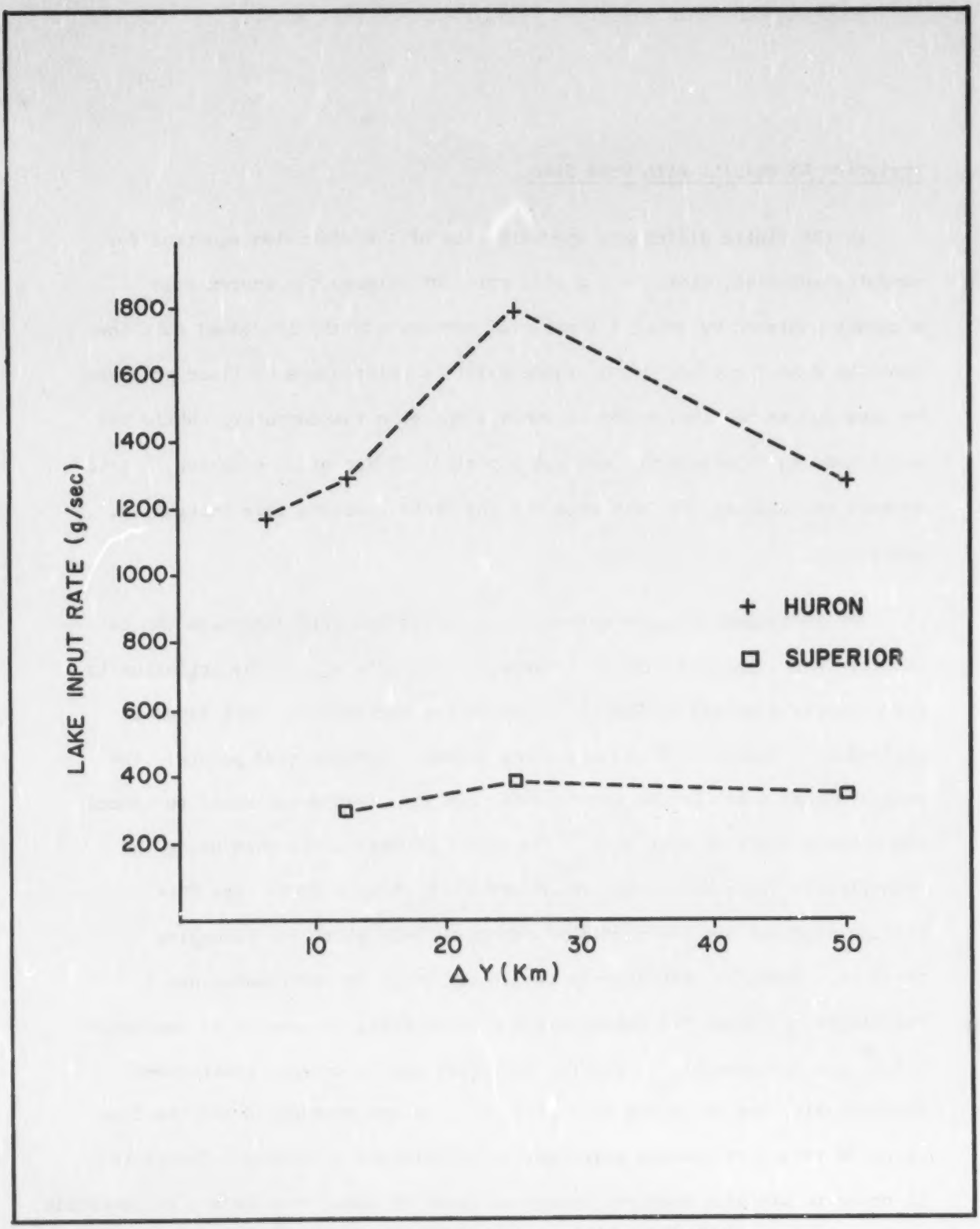

Figure 6.1: The Effect of Varying Grid Size on Lake Input Rate.

Variation Of Results With Original Source Height

Since the source height was selected somewhat arbitrarily, it was necessary to determine the sensitivity of the model to various source height selections. Computer runs 5 and 6 on Table 6.1 show that there was no variation of input into the lake with source height variations in the range of 1 to 10 m.

Variation Of Results With Deposition Velocity Over Land

The variation of the input into the lakes with the deposition velocity is shown by comparing computer runs 1, 10 and 11 in Table 6.1. The only other variable that changes in these runs is source height and that is known to produce no variation in input rate into the lakes over the given range. The results indicate that the rate of input increased significantly with a decrease from 1.0 to .1mm/s in deposition velocity over the land followed by a less rapid increase in input rate with a decrease from .1 to 0 mm/s in deposition velocity over land. The conclusion is that the results are sensitive to the selection of deposition velocity within certain ranges and that the somewhat arbitrary choice of deposition velocity over land used in this model for NO_2 could lead to a substantial error if the arbitrary choice varied from the true deposition velocity.

Variation Of The Results With The Addition Of A First Inversion Over Land And A Second Inversion Over Water

A comparison of computer runs 1 and 6 in Table 6.1 shows the effect of adding an inversion lid at 2km above the entire Great Lakes Basin. This lid was modeled as the first inversion over land and over water except in

the summertime when the relatively cool water created another inversion at 200m. The effect of adding an inversion at this height was to cause an insignificant change in input rate into the lakes. This can be attributed to the fact that for the distances of travel under consideration, the inversion was too high to allow reflection of pollutants to have any significant effect in increasing the pollutant concentration obtained without the inversion.

Variation Of The Results With The Addition Of A Background Concentration

A comparison of runs 6 and 8 on Table 6.1 indicates the effect of adding a background concentration. Adding a background concentration caused only a 9% increase in the input of NO_2 to Lake Huron while it caused a 160% increase in the input to Lake Superior. This is understandable since the concentrations of NO_2 over Lake Huron were high enough so that an additional 3 $\mu g/m^3$ background did not really have a significant effect. In contrast, the concentration of NO_2 over Lake Superior due to anthropogenic sources were so low that the addition of a 3 $\mu g/m^3$ background was extremely significant.

Variation Of The Results With A Change In The Method Of Background Concentration Addition

A theoretically more satisfying method of adding the background concentration was developed but only after the work was completed. For completeness, the new method is discussed and its effect on the final input values is considered. The new method is presented first and the old method is then discussed in light of the new.

The new method of background addition can be best explained by considering Figure 6.2. Source A represents the anthropogenic sources upwind of the interferring lake; source N_1 represents the natural sources upwind of the interferring lake; source N_2 represents the natural sources in the interferring lake, and source N_3 represents the natural sources between the interferring lake and the Upper Great Lake. The background concentration is defined here as that concentration at the receptor caused by all upwind natural sources. Therefore concentration wall A contained concentrations due to sources A and N_1. Concentration wall B contained concentrations caused by A, N_1, and N_2. Concentration wall C contained concentrations caused by A, N_1, N_2, and N_3. By definition the background concentration is a constant value at any receptor and is due to all upwind natural sources. Thus, the background concentration at concentration wall A due to source N, acting over a distance X_{1_A} is equal to the background concentration at concentration wall B due to source N_2 acting over a distance X_{2_B} and to source N_1 acting over a distance X_{1_B}.

As has been explained previously, this model converts the concentration grids into new source strength grids to allow a model to be used over several incremental distances. Thus, neglecting for the moment the natural sources, source A yields a source strength Q_A at concentration wall A, source Q_A yields a source Q_B at concentration wall B and source Q_B yields a source Q_C at concentration wall C. The difference between the new and old methods occurs when one considers how to include the natural sources in this incremental distance model. The new method takes the concentration at wall C resulting from

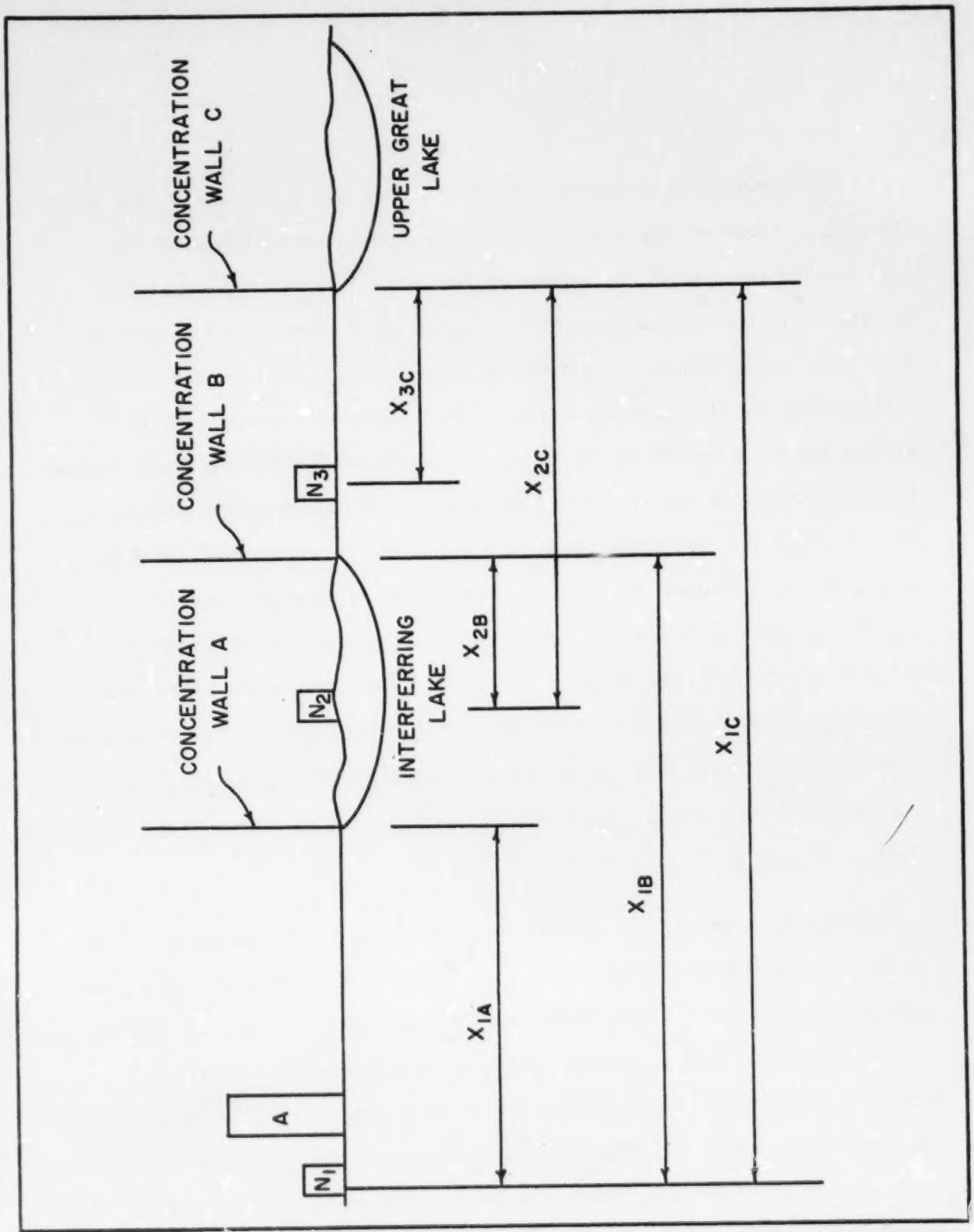

Figure 6.2: Schematic Illustration of the Inclusion of Natural Sources in an Incremental Diffusion Model.

source Q_B (which just includes anthropogenic source A) and adds the background concentration to it thus including at wall C the effect of N_1, N_2, and N_3. The sum of these two concentrations can then be converted to a new source strength, Q_{CN} and used to calculate the flux into the Upper Great Lake.

What has been done in this model is to add the background concentration to the concentration at wall A calculated using anthropogenic source A (thus including at effect of N_1) and to convert this to a new source strength Q_{AN}. Then the new source Q_{AN} which included the effects of A and N_1 was used to calculate a concentration at wall B. The background concentration was again added to the concentration at wall B (thus including the effects of N_1 and N_2) and the resulting concentration was converted to a new source strength Q_{BN}. The problem becomes obvious. The effect of natural source N_1 was included twice to get the concentration at wall B. First it was included in the new source strength Q_{AN} which was used in the model to calculate the concentration at wall B, and second, it was included in the background concentration which was added to the calculated concentration at wall B. This problem multiplies as one takes the next incremental step to wall C.

The new method adds the background concentration only at wall C. Thus only the effect of source A will be felt in each incremental step until the last step which is the determination of the concentration at wall C. Here, the background should be added and the effect of natural sources N_1, N_2 and N_3 will be felt only once as expected. This will actually change the input into Lake Huron little as shown in the previous section where runs 6 and 8 were compared but the input into Lake Superior will increase by some value less than 160% with this new method of considering background.

Variation Of The Predicted Input With The Correction Of A Model Error

In the development of the original model, a conceptual error was made which led to a sign error in the final flux equation. Unfortunately, all the work was finished before this error was discovered. Thus, in this section, the effect of this error is evaluated. The actual question of concern was what the effect of this error was on the final predicted flux. Looking at the expression for the flux, Equation 2.24, there are three exponential terms:

$$\text{Term 1} \rightarrow h \exp\left(-\frac{h^2}{2\sigma_z^2}\right)$$

$$\text{Term 2} \rightarrow (2H' - h) \exp\left(-\frac{(2H' - h)^2}{2\sigma_z^2}\right)$$

$$\text{Term 3} \rightarrow (2H' + h) \exp\left(-\frac{(2H' + h)^2}{2\sigma_z^2}\right)$$

In the erroneous model, Term 3 was negative instead of positive. The magnitudes of these three terms were evaluated for various input parameters and are recorded in Table 6.2. The source height, h, was valued at 10m as was done to acquire the final predicted inputs given in Table 6.9. In the first three columns, the third term is negligible in comparison to the others. The effect of changing the sign on Term 3 from positive to negative is seen to be potentially important only for the case of column 4. Actually, column 2 is most representative of the summer while column 3 is most representative of the other 3 seasons. Thus in the summer this error should theoretically have caused only a 2% lower predicted flux than reported while for the other seasons a 15% lower flux than reported. The calculation for the first percentage can be made as follows: 2% = (1 - (9.95 + .194 - .092)/(9.95 + .194 + .092))

These theoretical estimates of the error were actually checked (for the summer only) by running the corrected computer model for NO_2. The incorrect versus the correct flux is shown in Table 6.3. The correct flux is 2% higher

TABLE 6.2 : VARIATION OF THE TERMS IN THE FLUX EQUATION FOR VARIOUS INPUT CONDITIONS

	σ_z = 100m		σ_z = 1000m	
	H' = 2000m	H' = 200m	H' = 2000m	H' = 200m
TERM 1	9.95	9.95	9.999	9.999
TERM 2	0.	.194	1.39	361.
TERM 3	0.	.092	.917	376.

TABLE 6.3 : EFFECT OF THE SYSTEMATIC ERROR

	INCORRECT FLUX (kg/s)	CORRECT FLUX (kg/s)
SUPERIOR	.3	.298
HURON	.87	.896

for Huron as theory predicts while the correct flux is 2% lower for Superior. While this second result is not readily explained the point is that the error really has little effect on the model.

Variation Of The Results With The Inclusion Of Several Reflections In The Concentration Equation

The most complete expression of the concentration in an inversion trap is

$$C = \frac{Q}{u2\pi\sigma_y\sigma_z} \exp\left(-1/2\left(\frac{Y}{\sigma_y}\right)^2\right) \cdot \left\{\exp\left(-1/2\left(\frac{z-h}{\sigma_z}\right)^2\right) - Y \exp\left(-1/2\left(\frac{z+h}{\sigma_z}\right)^2\right) + \sum_{n=1}^{n=\infty} \left\{\exp\left(-1/2\left(\frac{z-(2nH'-h)}{\sigma_z}\right)^2\right) - Y \exp\left(-1/2\left(\frac{z+(2nH'+h)}{\sigma_z}\right)^2\right) + \exp\left(-1/2\left(\frac{z-(2nH'+h)}{\sigma_z}\right)^2\right) - Y \exp\left(-1/2\left(\frac{z+(2nH'-h)}{\sigma_z}\right)^2\right)\right\}\right\} \quad 6.1$$

The concentration equation used in this model, Equation 6.1, utilized only one reflection (n=1). The importance of each term in Equation 6.1 is shown in Table 6.4 for the special case of z=0. Under this condition, the exponential terms can be expressed in the form

$$\exp\left(-1/2\left(\frac{h \pm 2nH'}{\sigma_z}\right)^2\right)$$

or

$$\exp\left(-1/2\left(\frac{H'}{\sigma_z}\right)^2 \quad \left(\frac{h}{H'} \pm 2n\right)^2\right)$$

The variation of this later expression for various values of $\frac{H'}{\sigma_z}$ and $\frac{h}{H'}$ is shown in Table 6.4. Recall that for this research, the smallest value of H' was 200m in the summer and the source height, h, was 10m. Thus, h/H' was

TABLE 6.4: THE VALUE OF THE EXPONENTIAL TERMS FOR VARIOUS $\frac{H'}{\sigma_z}$, $\frac{h}{H'}$ and n

$\frac{H'}{\sigma_z}$	$\frac{h}{H'}$	n=0	n=1	n=-1	n=2	n=-2	n=3	n=-3	n=4	n=-4	n=5	n=-5
2.5	0.0	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2.5	0.5	.458	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.25	0.0	1.000	0.044	0.044	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.25	0.5	0.822	0.008	0.172	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
.625	0.0	1.000	0.458	0.458	0.044	0.044	0.001	0.001	0.000	0.000	0.000	0.000
.625	0.5	0.952	0.295	0.644	0.019	0.091	0.000	0.003	0.000	0.000	0.000	0.000
.2	0.0	1.000	0.923	0.923	0.726	0.726	0.487	0.487	0.278	0.278	0.135	0.135
.2	0.5	0.995	0.882	0.956	0.667	0.783	0.430	0.546	0.236	0.325	0.110	0.164

always between 0.0 and 0.5. Values of $\frac{H'}{\sigma_z} \geq 2$ were most representative of the conditions considered for all the seasons and consequently, one finds from Table 6.4 that no error was incurred by considering only one reflection (n=1).

COMPUTER OUTPUT SAMPLES

Tables 6.5 through 6.8 represent sample computer outputs for NO_2 concentration and flux at various lake edge coordinates for both Lakes Huron and Superior. The sample results were calculated using the input parameters specified under computer run 11 of Table 6.1. Recall that Table 6.1 was developed for summertime dispersion under a wind speed of 8.96 m/s and for a wind direction of 225°. The transformed x and y coordinates in Tables 6.5 through 6.8 are the downwind and crosswind coordinates respectively. Recall that with the wind from 225° instead of 270° for which the original coordinate system was developed, a coordinate transformation is necessary. The height in Tables 6.5 and 6.7 is the height above the ground at which the concentration was calculated.

Several conclusions can be drawn from these tables. Looking at Tables 6.5 and 6.7 , one can see that the concentration is essentially constant over height. This is reasonable considering the long distances of travel (up to 700 km) that one is concerned with since the Gaussian distribution degenerates into a constant valued distribution in the vertical as one moves farther and farther downwind. As a second consideration, it is noteworthy to discuss the high concentration of NO_2 at Sarnia shown on Table 6.5 . This high value is due to the very close and very strong downwind source of Detroit. A third point of discussion can be gleened by comparing Table 6.5

TABLE 6.5: PREDICTED NO_2 CONCENTRATIONS AT LAKE EDGE COORDINATES ALONG THE SOUTHERN PORTION OF LAKE HURON GIVEN 8.96 m/s WINDS AT 225°

Concentration ($\mu g/m^3$)	Height (m)	Transformed x coord (km)	Transformed y coord (km)	Location
13.0	0.0	1240.	-259.	*Actual Coordinates: (20, 13) @ 40 miles NE of Saginaw
12.9	20.0	1240.	-259.	
12.9	40.0	1240.	-259.	
12.9	60.0	1240.	-259.	
12.9	80.0	1240.	-259.	
12.9	100.0	1240.	-259.	
12.9	120.0	1240.	-259.	
12.8	140.0	1240.	-259.	
12.8	160.0	1240.	-259.	
12.7	180.0	1240.	-259.	
12.7	200.0	1240.	-259.	
39.4	0.0	1230.	-305.	Actual Coordinates: (20.4, 12.3) @ 60 miles E of Saginaw
39.4	20.0	1230.	-305.	
39.3	40.0	1230.	-305.	
39.2	60.0	1230.	-305.	
39.0	80.0	1230.	-305.	
28.8	100.0	1230.	-305.	
38.6	120.0	1230.	-305.	
38.3	140.0	1230.	-305.	
38.0	160.0	1230.	-305.	
37.7	180.0	1230.	-305.	
37.3	200.0	1230.	-305.	
161.0	0.0	1210.	-351.	Actual Coordinates: (21, 11.5) @ Sarnia, Ontario
160.0	20.0	1210.	-351.	
160.0	40.0	1210.	-351.	
160.0	60.0	1210.	-351.	
159.0	80.0	1210.	-351.	
158.0	100.0	1210.	-351.	
156.0	120.0	1210.	-351.	
155.0	140.0	1210.	-351.	
153.0	160.0	1210.	-351.	
151.0	180.0	1210.	-351.	
149.0	200.0	1210.	-351.	

*Actual coordinates found in Figure 3.1.

TABLE 6.6: THE PREDICTED FLUX OF NO_2 AT VARIOUS POINTS OF THE SURFACE OF LAKE HURON FOR 8.96 m/s WINDS AT 225°

Flux (ng/m^2 - s)	Transformed x coord (km)	Transformed y coord (km)
44.2	1240.	-337.
6.4	1270.	-300.
38.4	1310.	-337.
11.4	1270.	-225.
4.1	1310.	-262.
5.6	1350.	-300.
26.0	1310.	-187.
10.1	1350.	-225.
3.7	1390.	-262.
9.9	1310.	-112.
20.6	1350.	-150.
23.4	1390.	-187.
9.2	1420.	-225.
3.4	1460.	-262.
4.9	1350.	-175.
8.7	1390.	-112.
18.7	1420.	-150.
21.5	1460.	-187.
8.5	1500.	-225.

The total input into Lake Huron is 873 g/s

where

$$\text{total input} = \sum_{i=1}^{n} \frac{\text{FLUX (i)} \cdot \text{AREA OF LAKE}}{\text{NUMBER OF POINTS (N)}}$$

TABLE 6.7: PREDICTED NO_2 CONCENTRATIONS AT LAKE EDGE COORDINATES ALONG THE SOUTHERN PORTION OF LAKE SUPERIOR GIVEN 8.96 m/s WINDS AT 225°

Concentration ($\mu g/m^3$)	Height (m)	Transformed x coord (km)	Transformed y coord (km)	Location
4.66	0.0	1220.	198.	*Actual Coordinates: (13.7, 12.9) 110 km W. of Sault Ste. Maria
4.66	20.0	1220.	198.	
4.66	40.0	1220.	198.	
4.65	60.0	1220.	198.	
4.65	80.0	1220.	198.	
4.65	100.0	1220.	198.	
4.64	120.0	1220.	198.	
4.64	140.0	1220.	198.	
4.63	160.0	1220.	198.	
4.62	180.0	1220.	198.	
4.61	200.0	1220.	198.	
5.10	0.0	1250.	160.	Actual Coordinates: (14.6, 18.9) 87 km W. of Sault Ste. Maria
5.10	20.0	1250.	160.	
5.10	40.0	1250.	160.	
5.10	60.0	1250.	160.	
5.09	80.0	1250.	160.	
5.08	100.0	1250.	160.	
5.07	120.0	1250.	160.	
5.06	140.0	1250.	160.	
5.05	160.0	1250.	160.	
5.03	180.0	1250.	160.	
5.02	200.0	1250.	160.	
5.71	0.0	1320.	83.7	Actual Coordinates: (15.5, 18.8) 65 km W. of Sault Ste. Maria
5.71	20.0	1320.	83.7	
5.71	40.0	1320.	83.7	
5.71	60.0	1320.	83.7	
5.70	80.0	1320.	83.7	
5.69	100.0	1320.	83.7	
5.69	120.0	1320.	83.7	
5.68	140.0	1320.	83.7	
5.66	160.0	1320.	83.7	
5.65	180.0	1320.	83.7	
5.64	200.0	1320.	83.7	

*Actual coordinates found on Figure 3.1 .

TABLE 6.8: THE PREDICTED FLUX OF NO_2 AT VARIOUS POINTS ON THE SURFACE OF LAKE SUPERIOR FOR 8.6 m/s WINDS @ 225°

Flux (ng/m^2 - s)	Transformed x coord (km)	Transformed y coord (km)
5.65	1050.	450.
5.32	1090.	412.
4.01	1120.	375.
3.59	1160.	337.
3.54	1200.	300.
3.22	1240.	262.
2.93	1270.	225.
2.86	1310.	187.
5.09	1350.	150.
5.87	1390.	112.
.015	1200.	225.
.018	1240.	187.
5.92	1270.	150.
6.76	1310.	112.
4.62	1350.	75.
5.01	1120.	450.
4.74	1160.	412.
3.59	1200.	375.
3.21	1240.	337.
3.18	1270.	300.
2.91	1310.	262.
2.65	1350.	225.
2.59	1390.	187.
4.34	1240.	412.
3.29	1270.	375.
2.95	1310.	337.
2.93	1350.	300.
2.67	1390.	262.
3.05	1350.	375.
2.74	1390.	337.

Total input into Lake Superior is 300 g/s

where

$$\text{Total input} = \sum_{i=1}^{N} \frac{\text{FLUX (i) AREA OF LAKE}}{N}$$

with Table 6.7 . The concentrations at all points along Lake Huron are seen to be much higher than the concentrations along Lake Superior. This is explainable when one considers that Lake Huron is much closer to the large sources than is Lake Superior and when one considers that Lake Huron is closer to the centerline of the plumes from the large sources than is Lake Superior (for this particular wind direction of 225°). Finally, a comparison of Table 6.6 with Table 6.8 shows that the average point flux into Huron is larger than into Superior again due in this particular case to the alignment of Huron with the large sources.

QUANTIFICATION OF POLLUTANT INPUT BY DRY DEPOSITION INTO THE UPPER GREAT LAKES

The Yearly Input Of Pollutants Into The Upper Great Lakes

Table 6.9 shows the prediction of specific pollutant yearly inputs into the Upper Great Lakes by dry deposition processes. The total nitrogen input to Lake Superior is actually 72% particulate nitrates and 28% gaseous NO_2 while the total nitrogen input to Lake Huron is 60% particulate nitrates and 40% gaseous NO_2. The phosphorus input into both lakes is all particulate in form. The chlorides input for both lakes is 99.5% gaseous and .5% particulate in nature. The remaining 3 pollutants listed in Table 6.9 are all particulate in nature. The two pollutants yielding a significant input into the Upper Great Lakes in both gaseous and particulate forms are shown in Tables 6.10 and 6.11 where the quantity of each pollutant input by form is shown.

Seasonal Variation Of Input Into The Upper Great Lakes

Tables 6.12 and 6.13 show the variation of pollutant input into the Upper Great Lakes as a function of season. The fall and winter seasons were

TABLE 6.9 : FINAL PREDICTIONS OF YEARLY POLLUTANT INPUT INTO THE UPPER GREAT LAKES IN Mg/YR

POLLUTANT	SUPERIOR	HURON
Total Nitrogen	11,300	20,000
Total Phosphorus	5,860	8,730
Chlorides	534,000	792,000
Total Silica	17,800	26,500
Total Dissolved Solids	102,000	151,000
Pesticides	3.3	3.6

TABLE 6.10: GASEOUS AND PARTICULATE CONTRIBUTIONS TO THE POLLUTANT BURDEN OF LAKE SUPERIOR

	INPUT (Mg/YR)	
POLLUTANT	GASEOUS	PARTICULATE
Total Nitrogen	3,160	8,150
Chlorides	531,000	2,650

TABLE 6.11 : GASEOUS AND PARTICULATE CONTRIBUTIONS TO THE POLLUTANT BURDEN OF LAKE HURON

	INPUT (Mg/YR)	
POLLUTANT	GASEOUS	PARTICULATE
Total Nitrogen	7,900	12,100
Chlorides	788,000	3,940

TABLE 6.12: SEASONAL VARIATION OF POLLUTANT INPUT INTO LAKE SUPERIOR

POLLUTANT	SEASONAL INPUT (Mg/YR)		
	SPRING	SUMMER	FALL & WINTER
Total Nitrogen	2,470	1,590	7,260
Total Phosphorus	1,230	549	4,080
Chlorides	112,000	49,800	372,000
Total Silica	3,750	1,670	12,400
Total Dissolved Solids	21,400	9,600	71,000
Pesticides	1.077	1.08	1.16

TABLE 6.13: SEASONAL VARIATION OF POLLUTANT INPUT INTO LAKE HURON

	SEASONAL INPUT (Mg/YR)		
POLLUTANT	SPRING	SUMMER	FALL & WINTER
Total Nitrogen	4,460	2,980	12,600
Total Phosphorus	1,730	490	6,510
Chlorides	157,000	44,600	591,000
Total Silica	5,250	1,490	19,800
Total Dissolved Solids	30,000	8,520	113,000
Pesticides	1.18	.535	1.9

analyzed together since their stabilities and inversion lid heights were the same (see Table 4.2) and thus, only one value representing the input for both seasons was attained.

There are two major conclusions to be drawn from Tables 6.12 and 6.13 . First, the input of pollutants in the summer into the Upper Great Lakes is less than the input in the spring despite the fact that the summer had more dry hours than the spring. Second, the input of pollutants in the summer and spring taken together is less than the input of pollutants in the fall and winter taken together, again despite the fact that the summer and spring had more dry hours than the fall and winter. The reason for these conclusions can be understood by considering the equation for caluclating the seasonal input per unit area of lake surface, I_s:

$$I_s = \sum_{i=1}^{8} \sum_{j=1}^{4} \text{seasonal flux } (i, j) \cdot \text{seasonal dry time } (i, j)$$

where the first summation from i=1 to i=8 represents the 8 wind direction categories and the second summation j=1 to j=4 represents the 4 wind speed categories considered in the model. It happens that the seasonal variation of yearly input is directly related to the seasonal variation of flux and that the seasonal variation of dry time does not alter this direct relationship.

Furthermore, the seasonal variation of flux can be correlated to the seasonal variation of stability. The summer atmosphere was most stable, the spring yielded a slightly stable atmosphere, and the fall and winter both displayed a neutral atmosphere. The suggestion is that, for a lake with an inversion layer above, the more the atmosphere tends toward unstability, the greater the flux, and consequently, the input of pollutants into the lake.

Seasonal Variation Of Total Particulate Input With Size Range

Tables 6.14 and 6.15 show the seasonal variation of the total particulate input, both soluble and insoluble, with size range. The total particulate input into Lake Superior is equal to the sum of all the values in Table6.14. Likewise, the total particulate input into Lake Huron is the sum of all the values in Table 6.15 .

The Fraction Of The Total Atmospheric Burden of Pollutants Deposited Into The Upper Great Lakes

The total NO_2 gas emitted from anthropogenic sources in the Great Lakes area in 1973 was 9×10^6 Mg; the total particulate emitted from anthropogenic sources was 7×10^6 Mg, and the total pesticides emitted were 7×10^4 Mg. By dividing the value representing the input of the above pollutants into the Upper Great Lakes by the above values, an estimate of what percentage of the pollutants emitted into the atmosphere is deposited by dry deposition processes into the Upper Great Lakes was obtained. These percentages are not exact since the input into the lakes is actually composed of contributions from both natural and anthropogenic sources while the above numbers represent only anthropogenic sources. The percentages of the NO_2 gas emitted into the atmosphere that are deposited into Lakes Huron and Superior are .08% and .03% respectively. The percentages of total particulates emitted into the atmosphere that are deposited into Lakes Huron and Superior are 10.4% and 7.0% respectively. Finally, the percentages of pesticides emitted into the atmosphere that are deposited into Lakes Huron and Superior are .005% and .004% respectively.

TABLE 6.14: VARIATION OF SEASONAL PARTICULATE INPUT (Mg/YR) INTO LAKE SUPERIOR WITH SIZE

PARTICULATE SIZE RANGE	SPRING	SUMMER	FALL & WINTER
.01 - .33μm	39,600	3,590	119,000
.33 - 1.5μm	30,000	18,800	86,900
1.5 - 40μm	37,400	25,300	149,000

TABLE 6.15: VARIATION OF SEASONAL PARTICULATE INPUT (Mg/YR) INTO LAKE HURON WITH SIZE

PARTICULATE SIZE RANGE	SPRING	SUMMER	FALL & WINTER
.01 - .33μm	55,300	3,260	191,000
.33 - 1.5μm	43,200	17,500	140,000
1.5 - 40μm	51,900	21,800	235,000

CONCLUSIONS AND RECOMMENDATIONS

The conclusions to be drawn from this research are:

1. The yearly input of all the pollutants considered was larger for Lake Huron than for Lake Superior by factors varying from 1.1 to 1.9.

2. 20% of the particulate emitted into the atmosphere was deposited into the Upper Great Lakes while < 1% of the NO_2 gas and pesticides emitted were deposited into the Upper Great Lakes.

3. The input of pollutants into the lake in the summer was less than the input in the spring and the combined spring and summer inputs were less than the combined fall and winter inputs.

4. The more the atmosphere over a lake with an inversion layer above tends toward unstability, the greater the flux of pollutants into the lake.

5. The final pollutant input value is sensitive to the deposition velocity both over land and water.

6. Pesticide input from the atmosphere into the Upper Great Lakes by dry deposition processes is negligible. This is due to the small source strengths, the large area over which the sources were spread, and the large distances of travel for pesticides.

7. The total nitrogen input to Lake Superior was 72% particulate nitrates and 28% gaseous NO_2. The total nitrogen input to Lake Huron was 60% particulate nitrates and 40% gaseous NO_2.

8. 99.5% of all chloride input into both Upper Great Lakes was gaseous in form.

9. Only 79% of the total yearly hours was classified as dry yearly hours. This reduced seasonally, in order of dryness, to summer, for which 85% of the season was dry, fall for which 79% of the season was dry, spring for which 78% of the season was dry and winter for which 76% of the season was dry.

10. The yearly dry time allotment according to wind speed category resulted in the wind being less than 3.1 m/s during 37% of the time, between 3.1 and 5.8 m/s during 46% of the time between 5.8 and 8.1 m/s during 13% of the time and greater than 8.1 m/s during only 4% of the total yearly dry time.

11. The yearly dry time allotment according to wind speed category resulted in the following percentages:

a) from N 12% of the time
b) from NE 5% of the time
c) from E 17% of the time
d) from SE 4% of the time
e) from S 15% of the time
f) from SW 14% of the time

g) from W 25% of the time

h) from NW 8% of the time

The fact that the winds were from the S to W quadrant 54% of the time caused a higher yearly atmospheric pollutant burden in the Upper Great Lakes than if the predominant wind direction were from another quadrant. This is because the closest large sources are located in the S to W quadrant.

There are several refinements which would afford estimates more accurate than the current "order of magnitude":

1. Take the known estimate of 4 $\mu g/m^3$ for background NH_3 concentrations (Rasmussen, Taheri, Kabel, 1974), and calculate the input of NH_3 into the Upper Great Lakes from natural sources by building a wall of concentrations of 4 $\mu g/m^3$ at the edge of each Upper Great Lake and forming new sources at this wall.

2. The background concentration should be added at the concentration wall located on the upwind side of the Upper Great Lake of concern. This will enable the natural sources to be accounted for only one time.

3. The data found in the literature suggests large amounts of gaseous chlorides in the atmosphere. These gaseous chloride sources need to be located and quantified. The prediction of gaseous chloride input into the Upper Great Lakes can then be handled by calculating an appropriate value for k_ℓ and proceeding in a manner identical to that of NO_2.

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